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**ELECTRON SPIN RESONANCE STUDIES OF
PHOTO-OXIDATION BY METAL IONS**

by

D. GREATOREX

**A dissertation submitted in part fulfilment
of the requirements for the degree of
Doctor of Philosophy at the University of Warwick**

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ABSTRACT

ABSTRACT

The e.s.r. technique has been applied to the study of primary processes occurring during photo-induced electron transfer reactions between metal ions and organic substrates. Photolysis of deoxygenated solutions of ceric perchlorate and ceric ammonium nitrate in alcoholic, aqueous alcoholic and water/alcohol/acetonitrile solutions at 77°K by light of wavelength $> 300\text{ nm}$ leads to formation of radicals derived from the alcohol. Primary alcohols, RCH_2OH , yield RCHOH but secondary alcohols, R_2CHOH , yield R^{\bullet} in addition to, and sometimes to the exclusion of, R_2COH . Tertiary alcohols always give an alkyl fragment, e.g. $\text{C}_2\text{H}_5^{\bullet}$, from 1,1-dimethylpropan-1-ol. Allylic alcohols produce the corresponding hydroxyallyl radical and 1,2-diphenylethanol gives a spectrum of benzyl radical, indicating C-C cleavage. The mode of photo-oxidation by Ce^{IV} clearly parallels that of the corresponding thermal reaction.

The primary process in the photo-oxidation of a large number of carboxylic acids, RCO_2H , by Ce^{IV} , has also been studied in a similar manner. The most general pathway is that of oxidative decarboxylation to give the readily characterised R^{\bullet} , although alternative routes are found with lactic and acetic acids. Well-resolved spectra of R^{\bullet} are recorded for $\text{R}^{\bullet} = \text{cyclopropyl, cyclobutyl, allyl, vinyl, CH}_2\text{F, CO}_2\text{H and CH}_2\text{NH}_3$ amongst others, and H^{\bullet} and D^{\bullet} atoms display interaction with solvent protons. Secondary reactions are found in some cases, especially with two dicarboxylic acids which yield initially the spectra of $(\text{CH}_2)_n\text{CO}_2\text{H}$ ($n = 1$ or 2); these decay on warming, but renewed photolysis then produces either CH_3^{\bullet} (for $n = 1$) or $\text{C}_2\text{H}_5^{\bullet}$ (for $n = 2$). Mechanisms of these processes are discussed. The final section of the Ce^{IV} work deals with primary processes occurring during photo-oxidation of a variety of organic compounds, at 77°K , classified by functional groups. Aldehydes, RCHO , and aldehyde hydrates, RCH(OH)_2 , are oxidised to RCO and RC(OH)_2 respectively at 77°K ; thermal and photochemical reactions of RCO are observed at higher temperatures. Ketones produce either the alkyl radical R^{\bullet} from RCOR^{\bullet} or the radical derived by abstraction of a hydrogen atom from the methylene or methine groups adjacent to the carbonyl group; in some cases both radicals are discernable. Esters also undergo C-H or C-C fission processes, depending on the degree of substitution of the R fragment of

$\text{RCO}_2\text{R}'$, whilst amides yield spectra dependent on the degree of substitution of the nitrogen atom. Ethers yield the radical formed by α -hydrogen atom abstraction. Methylmethacrylate yields a vinylic monomer radical at 77°K which induces polymerisation at 175°K to give the familiar polymethylmethacrylate radical.

The technique is further applied to electron transfer reactions between U^{VI} and a selection of organic substrates. Alcohols and ketones behave in a similar manner as with Ce^{IV} but acids ($\text{RCH}_2\text{CO}_2\text{H}$) yield as the major component, RCHCO_2H . The rôles of U^{V} and U^{IV} are discussed with respect to subsequent reactions of the primary radicals formed.

The final section of the work concerns the design of a continuous flow system for studies down to 180°K . Well-resolved e.s.r. spectra are obtained when solutions of metal ions in organic solvents containing appropriate substrates are subjected to intense photolysis in this flow system. The reactions between Ce^{IV} and alcohols, U^{VI} and alcohols have been studied. Ce^{IV} produces R^\cdot from RCH_2OH whilst U^{VI} yields RCHOH^\cdot ; both mechanisms are discussed. Photo-oxidation of benzoic acid by a variety of metal ions yields the benzophenone ketyl radical, confirmed by flash photolysis experiments.

CHAPTER 1
INTRODUCTION

1. INTRODUCTION

1.1 Spectroscopy and Photochemistry of Transition Metal Ions in Solution

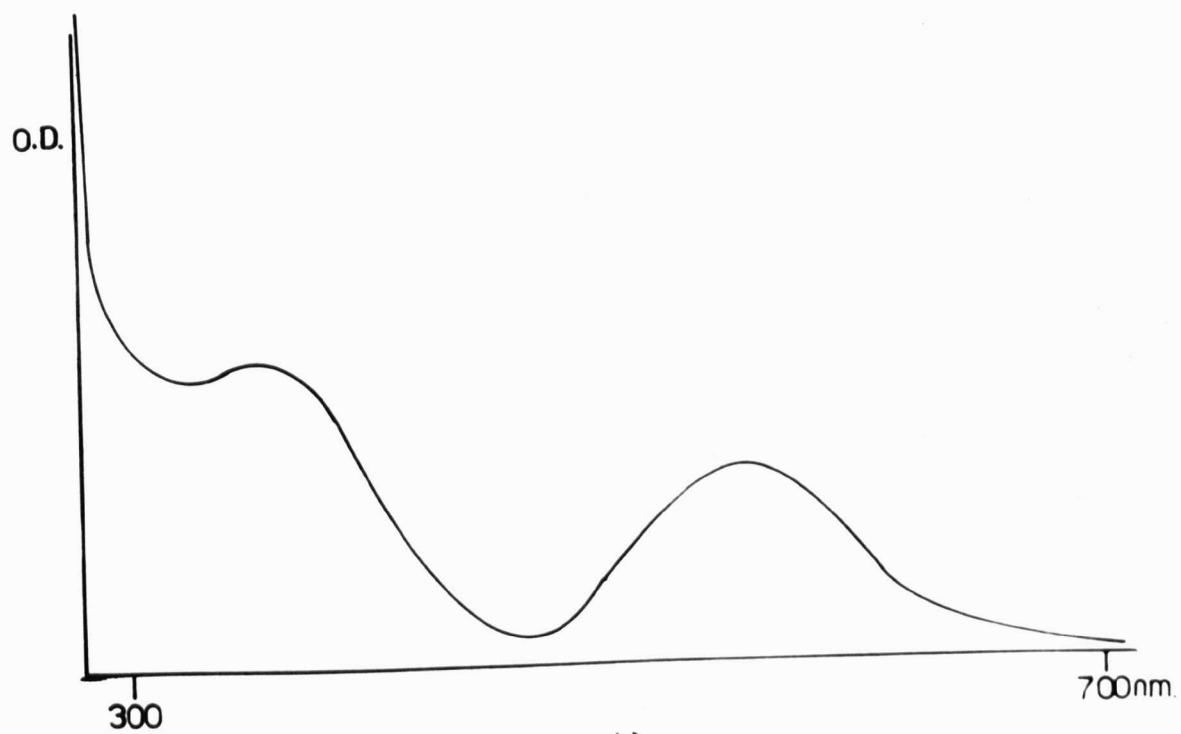
Transition metal complexes in solution are, in general, sensitive to light and undergo many recognisable transformations when irradiated with visible or ultra-violet (u.v.) light and a number of books and reviews have been published on the subject. Wehry¹ discusses complexes of Co^{III} and Cr^{III} and also oxalato complexes of some other transition metal ions. Valentine² reviews only Co^{III} and Cr^{III} although in greater detail. The most comprehensive review comes from Adamson et al.³ who cover the literature of inorganic photochemistry up to the end of 1967. The standard inorganic text of Basolo and Pearson⁴ refers to the photochemistry of Cr^{III} and Co^{III} complexes, and the book by Rabinowitch and Belford⁵ deals specifically with the rather complex photochemistry of the uranyl ion. The only recent comprehensive text on the subject of inorganic photochemistry, by Balzani and Carassiti,⁶ is complete up to the end of 1969.

The spectra of transition metal ions in solution consist of two different types of absorption. One occurs in the visible region and consists of one or more bands of low intensity ($\epsilon < 100 \text{ l mol}^{-1} \text{ cm}^{-1}$). The other type of absorption is found at shorter wavelengths and consists of a strong band or sometimes simply an increasing absorption into the u.v. region (ϵ from 2×10^3 to $2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). A typical example is shown in fig. 1a. The origin of these bands can be explained in the following manner, for example, for a transition metal ion in an octahedral ligand field. It is possible to construct a molecular orbital (MO) representation (fig. 1b) using the 3d orbitals of the metal and σ and π orbitals of the six ligands.

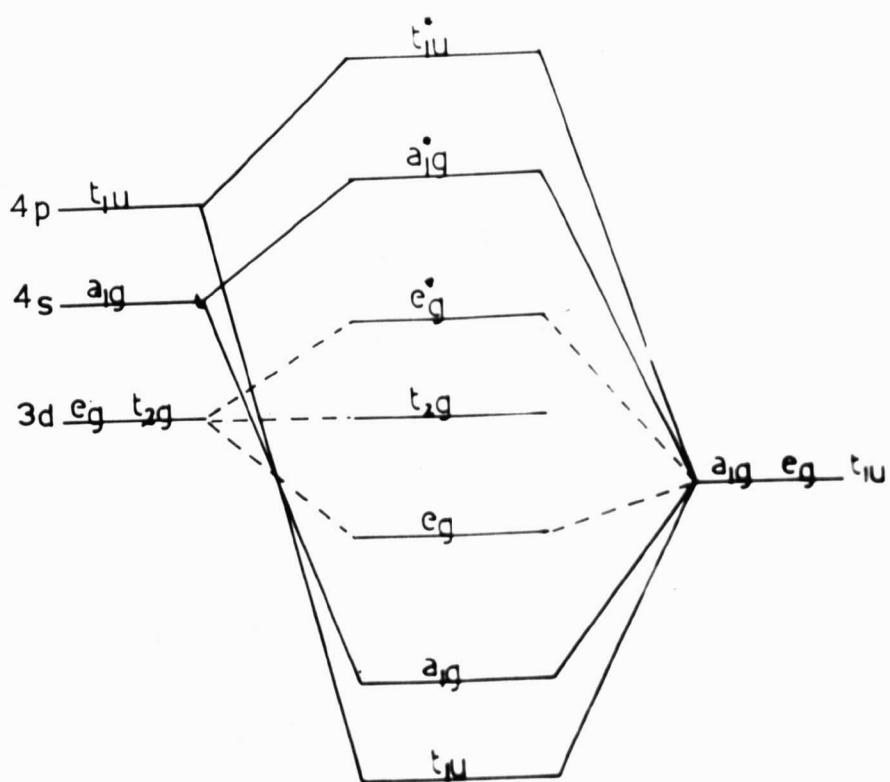
(a) Ligand Field Bands. The lowest energy transitions are of the type $t_{2g} \rightarrow e_g^*$; these are by nature Laporte-forbidden ($g \leftrightarrow g$) and they appear as weak absorptions. Such transitions involve promoting an electron from an orbital directed away from the ligands (t_{2g}) to an orbital directed more towards them (e_g^*). These are called ligand field or d-d transitions. Excitation in these bands will result in weakening the metal-ligand bond,

FIGURE 1

- (a) Typical transition metal complex absorption spectrum**
- (b) Construction of molecular orbitals for octahedrally co-ordinated complexes of non- π bonding ligands using metal 3d, 4s, 4p orbitals**



(a)

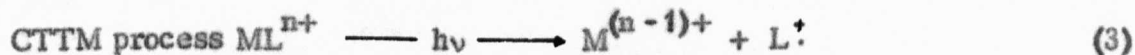
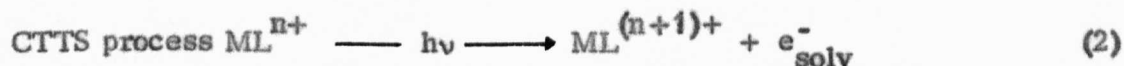
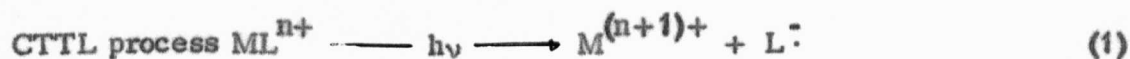


(b)

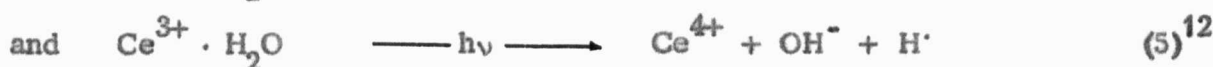
giving rise to various substitution, isomerisation and racemisation processes in solution; for example, photolysis of $\text{Co}(\text{CN})_6^{3-}$ in aqueous solution^{7, 8, 9} leads to $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$, and a five-coordinated species, $\text{Co}(\text{CN})_5^{2-}$ is proposed as the reaction intermediate. Photolysis of certain oxalato complexes, e.g. $\text{Cr}(\text{CO}_4)_3^{3-}$, results in racemisation.¹⁰

(b) Charge Transfer Bands. The absorptions appearing at shorter wavelengths are due to charge-transfer (CT) transitions. These are neither spin- nor Laporte-forbidden and are consequently very much stronger than the corresponding ligand-field transitions. They involve radial displacement of an electron between two orbitals, one close to the metal atom and the other close to the ligand. During photo-excitation, the metal atom will therefore change its formal oxidation state by ± 1 , depending on whether :

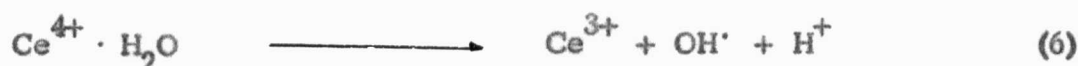
- (i) charge is moved from the metal atom either towards a ligand (a charge-transfer-to-ligand or CTTL process) or towards solvent molecules (a charge-transfer-to-solvent or CTTS process) or,
- (ii) charge is moved towards the metal atom in a charge-transfer-to metal or CTTM process. These possibilities may be expressed as follows :



The mode of photo-decomposition is dependent both on the nature of the central metal ion and on its associated ligands. If M is oxidising and L is oxidisable, then reaction (3) will occur, whilst if M is reducing and L is oxidising, then reaction (1) becomes possible. Generally reaction (3) is commoner than reaction (1) and the latter is given only by some low-valent hydrated cations, for example :



In contrast, the reaction



is far more photochemically efficient, with $\phi_{254} = 0.15^{12}$ compared with $\phi_{254} = 0.0003$ for reaction (5). Certain cyano complexes are thought to be photoreducing in character, and flash photolysis experiments with $\text{Mo}(\text{CN})_8^{4-}$ demonstrated photoelectron production,¹³ viz.



Many examples of reaction (3) have been reported;³ oxalato-complexes of metal ions are very prone to this behaviour¹⁴ and the ferrioxalate actinometer is a practical example,¹⁵



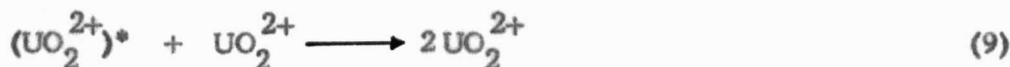
As it is the purpose of this work to study some photochemical reactions of the type (3) exhibited by UO_2^{2+} and Ce^{IV} ions in solution, a detailed discussion of their chemistry follows.

1.2 Oxidation-Reduction Chemistry of the Uranyl Ion

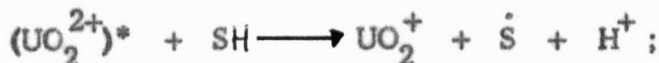
The formal electrode potential for the $\text{U}^{\text{VI}}/\text{U}^{\text{V}}$ couple is 0.063 volts¹⁶ and its thermal reactions are consequently limited to those with strong reducing agents like e^-_{solv} ¹⁷ and Cr^{II} .¹⁸ U^{VI} is, however, very photosensitive and exhibits strong oxidising properties upon photolysis. The absorption spectrum of the UO_2^{2+} ion in dilute perchloric acid shows a large number of overlapping bands of low extinction ($\epsilon \sim 10$) between 500 and 330 nm and an increasing absorption ($\epsilon \sim 1200 - 2000$) below $\lambda = 300$ nm. Theoretical calculations on this "simple" system by Bell and Biggers,¹⁹ using a sophisticated curve-fitting programme, show that the spectrum can be analysed in terms of two main absorptions assigned to the transitions to triplet states, containing twenty-one overlapping bands, and the combined u.v.-visible spectrum of the UO_2^{2+} aq. ion represents a series of vibronic transitions having progressively increasing oscillator strengths. Charge-transfer bands have been observed with com-

plexing ligands like oxalate²⁰ and thiocyanate²¹ and it seems likely that complexes of UO_2^{2+} with organic acids also show C-T bands.²²

The uranyl ion is amongst the few inorganic ions that exhibit a fluorescence spectrum. The fluorescence spectrum was first examined by Stokes²³ in 1853 who observed the band structure of the emission from a uranyl nitrate crystal. Mathematical resolution of the solution spectrum¹⁹ shows six bands within the 450 - 600 nm region, and emission occurs from the lowest excited singlet state to vibrational levels of the ground state. Because of the weakness of absorption bands of UO_2^{2+} ion in solution, fluorescence lifetimes are long, e.g. ca. 5×10^{-4} sec for UO_2^{2+} in sulphuric acid.²⁴ The fluorescence yield²⁵ is high (0.8) at low UO_2^{2+} concentrations ($\sim 10^{-4}$ M), decreasing to 0.2 with increasing UO_2^{2+} concentration (1 M) due to self-quenching, viz.



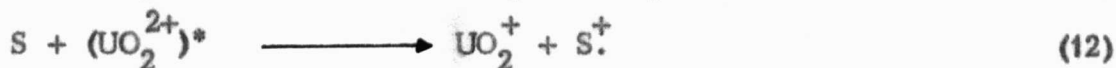
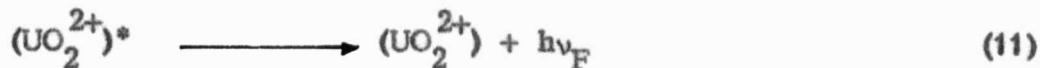
Many substances are known to quench uranyl fluorescence and much work has been done on quenching by I^- , Cl^- and organic acids,²⁶ to give products derived from electron transfer, viz.

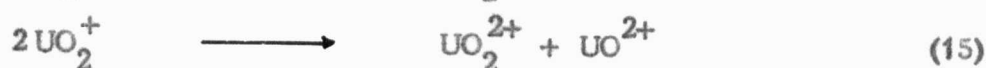


for example, in the case of $\text{S} = \text{I}^-$ the resulting product is I_2 from the combination of two iodine atoms.²⁷

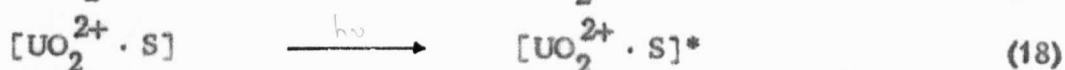
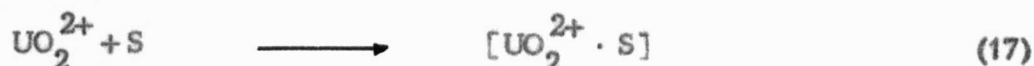
Two mechanisms have been proposed for oxidation by photo-excited uranyl ions which may be represented by the following schemes, where S is any substrate molecule.

- (i) Kinetic encounter mechanism, whereby a uranyl ion in an excited electronic state collides with a substrate molecule to produce a radical intermediate and a U^{V} species, viz.





- (ii) Complex formation mechanism, in which prior formation of a complex between a uranyl ion and a substrate molecule(s) is necessary, followed by an internal electron transfer on photo-excitation, viz.

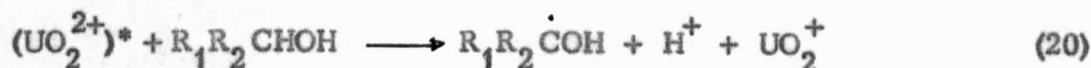


followed by reactions (13) - (16) as before.

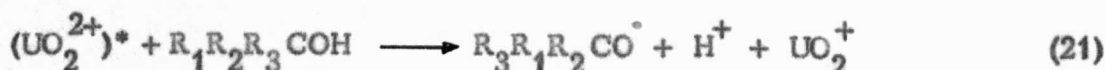
There is spectrophotometric evidence²⁸ for distinct complexes between UO_2^{2+} and malonic acid (1:1 complex) and succinic acid (1:2 complex). Stability constants for 1:1 and 1:2 complexes of uranyl ions and various carboxylic acids, including formic, succinic, propionic, crotonic, thiomalic and pyruvic acid,²⁹ lie within the range $180 - 10^4$. I.r. studies³⁰ of UO_2^{2+} ion dissolved in a number of liquid esters and ketones indicate bonding to the carbonyl group.

Because of the instability of the radical, molecular and ionic intermediates involved, most work on UO_2^{2+} photochemistry has been carried out by end-product analysis, steady-state photochemistry and fluorescence quenching. On this basis, for example, the following mechanism is proposed for the photo-oxidation of butanols³¹ by UO_2^{2+} ion.

- (i) Butanols with α -H atoms :



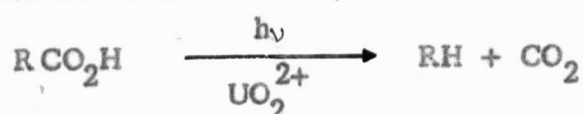
- (ii) Tertiary butanol :



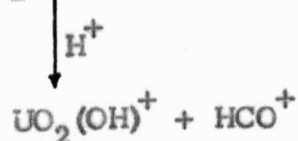
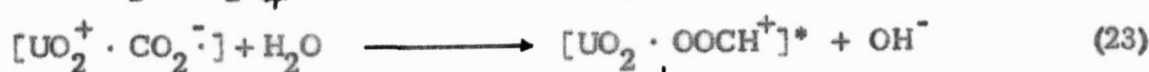
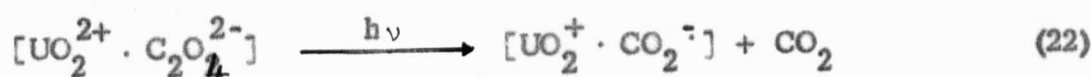
The relative reactivities of the alcohols (t-butanol is an order of magnitude less reactive than n-, i- and s-butanols) indicates that C - H bond fission is effected

more readily than O - H bond fission. Analogous mechanisms have been proposed for the photo-oxidations of methanol³² and ethanol.³³ It is interesting to note that very large quantum yields (ϕ ca. 5 - 40, depending on λ) for the production of acetaldehyde (from ethanol) have been reported, giving an indication of the complexity of the reactions involved.

The photosensitivity of UO_2^{2+} ion towards organic acids was noted first in 1805³⁴ with solutions of oxalic acid, and this particular system has been developed to provide a reliable chemical actinometer.³⁵ In all cases decomposition of acids leads to production of carbon dioxide and usually a hydrocarbon (except in the cases of formic and oxalic acids), viz.



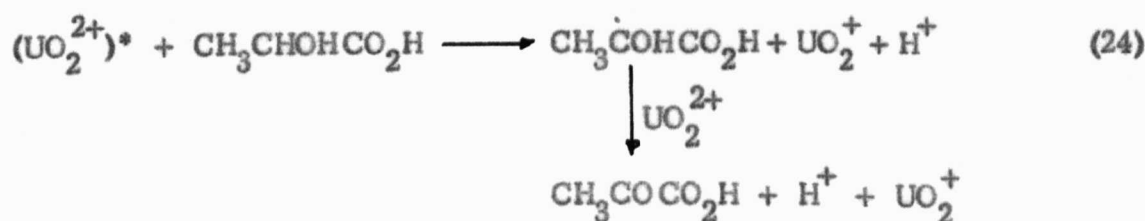
Both "kinetic encounter" and "complex formation" mechanisms (equations (12) and (17)) are plausible and have been proposed for these oxidations. The oxidation of oxalic acid³⁶ proceeds without major loss of U^{VI} and with formation of formic acid, and this has led to the following mechanism by Heidt.³⁷



A number of authors³⁸ have proposed a mixed mechanism in which both "kinetic encounter" and "complex formation" mechanisms operate in parallel and the overall reaction is the sum of these separate reactions.

It is postulated that the oxidation of lactic³⁹ acid by uranyl ions to acetaldehyde, carbon dioxide, pyruvic acid and U^{IV} proceeds via both mechanisms, the pathway, and consequently the product distribution, depending on the pH of the system, viz.

(i) $\text{pH} < 1$ "Kinetic encounter mechanism"



(ii) pH > 1 "Complex formation mechanism"

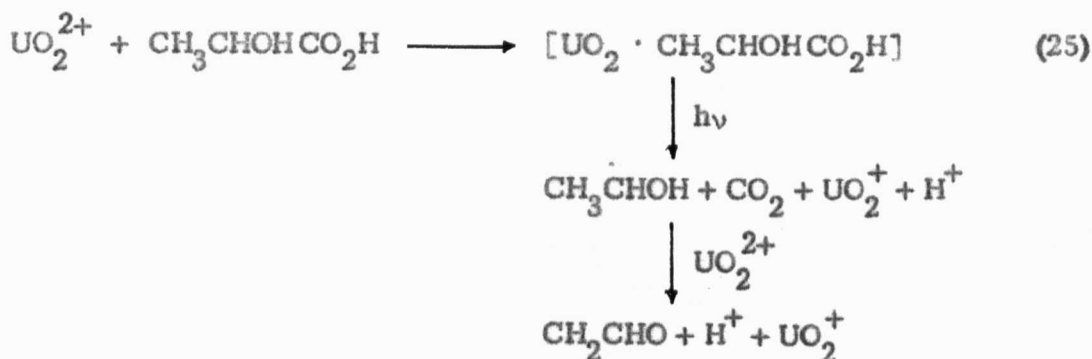
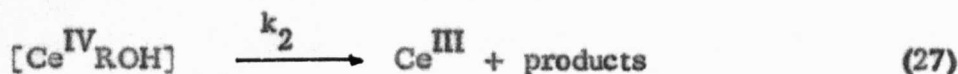
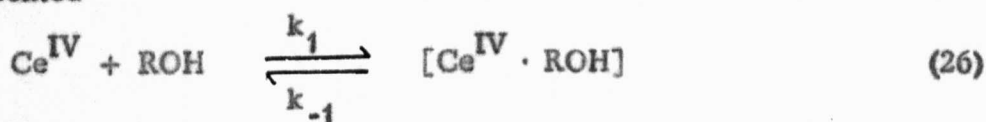


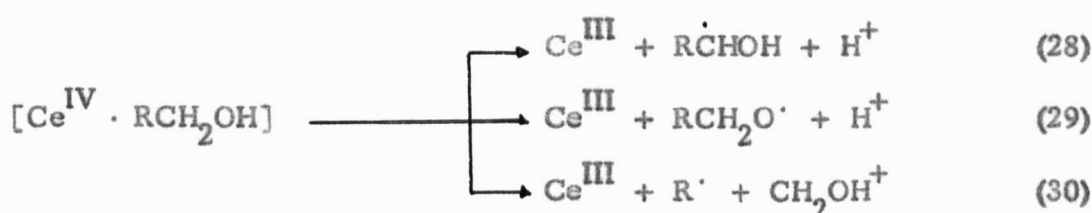
Photo-oxidations of halo acids, aromatic acids and thio acids⁴⁰ by UO_2^{2+} have been reported, in addition to those of aldehydes⁴¹ and sugars,⁴² without real resolution of the primary processes. There is one brief report each of an e.s.r.⁴³ and a flash photolysis⁴⁴ examination of an oxidation by UO_2^{2+} ions, i.e. that of oxalic acid, but neither of these have been investigated further hitherto.

1.3 Oxidation-Reduction Chemistry of the Ceric Ion

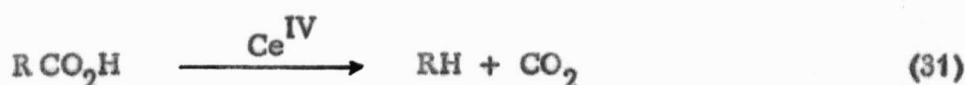
Ce^{IV} is a very powerful one-electron oxidising agent, the potential for the $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$ couple in perchloric acid being 1.7 volts,¹⁶ i.e. it is capable of oxidising water. Its oxidising properties are enhanced by light, yet the resulting reactions seem to closely parallel the corresponding thermal reactions. Ce^{IV} exhibits no fluorescence spectrum and because it is a d^0 system, it has no ligand bands in its absorption spectrum; however, Ce^{IV} -substrate complexes are evident from the appearance of a red shift in the visible spectrum upon adding alcohols to Ce^{IV} solutions in perchloric and nitrate media. Stability constants have been measured for ceric perchlorate-⁴⁵ and ceric ammonium nitrate-⁴⁶ alcohol complexes, lying within the range 0.8 for benzyl alcohols to 14 for cyclic and tertiary alcohols. In its most simple form the thermal oxidation of alcohols may be represented



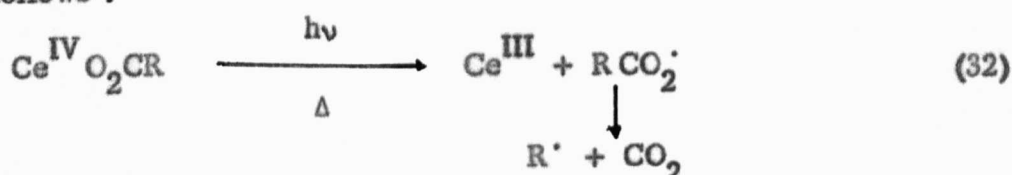
Such a system obeys Michaelis-Menten kinetics with k_2 being rate determining. Alcohols are oxidised to carbonyl compounds, e.g. ethanol and t-butanol are oxidised to acetaldehyde and acetone respectively.^{47, 48} Kinetic studies have been carried out on many different alcohols and the following mechanisms have been proposed for the slow step (27).



and reactions involving C - H cleavage and O - H cleavage have been proposed in the cases of methanol,⁴⁹ ethanol,⁴⁷ isopropanol⁵⁰ and other primary and secondary alcohols. Reaction (30) involving C - C cleavage has only been reported for the Ce^{IV} oxidation of 1,2-diaryl alcohols;⁵¹ however, this type of reaction is known to occur during oxidations of certain alcohols by Co^{III} ,⁵² Cr^{VI} ,⁵³ Pb^{IV} ,⁵⁴ and V^{V} .⁵⁵ Simple aliphatic acids are resistant to Ce^{IV} sulphate oxidation in refluxing aqueous solutions of dilute sulphuric acid. They do, however, react slowly with Ce^{IV} perchlorate in perchloric acid⁵⁶ to produce CO_2 and a hydrocarbon, viz.



Detailed work by Kochi et al.⁵⁷ on the oxidative decarboxylation of aliphatic acids by Ce^{IV} acetate shows that the thermal and photochemical decompositions proceed as follows :

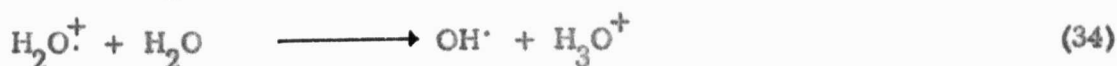
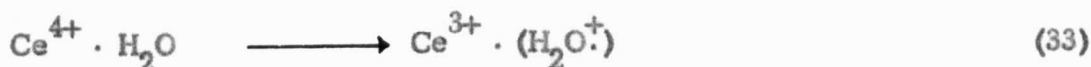


The existence of radical intermediates was suggested by radical scavenging experiments using Cu^{II} and end-product analysis. α -Hydroxy⁵⁸ acids, malonic⁵⁹ and oxalic acids⁶⁰ are, in comparison, readily oxidised thermally. Stopped-flow experiments on the oxidation of thio⁶¹ acids by Ce^{IV} indicate the formation of RS as a reactive intermediate. Ce^{IV} oxidises ketones and aldehydes with complicated stoichiometry and secondary reactions complicate the kinetics. The production of the phenoxy and other aryloxy radicals from phenols has been demonstrated in continuous flow e.s.r. studies,⁶²

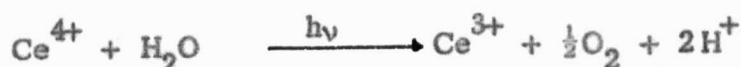


Reported photochemical reactions are much fewer and are concerned mainly with water,⁶³ carboxylic acids⁵⁷ and some inorganic ions like NO_3^- and $\text{Tl}(\text{I})$.⁶⁴ Differing mechanisms have been proposed for the photo-decomposition

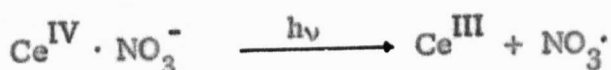
of Ce^{IV} solutions in nitrate, sulphate and perchlorate media. Hayon et al,⁶⁵ on the basis of flash photolysis experiments with Ce^{IV} in nitrate, sulphate and perchlorate solutions and also Moorthy and Weiss,⁶⁶ from e.s.r. experiments on photolysed Ce^{IV} perchlorate ices at 77°K , suggest that the primary photo-chemical act is electron transfer to the Ce^{IV} ion from its hydration sphere, viz.



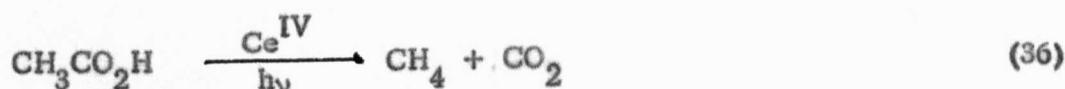
giving an overall reaction



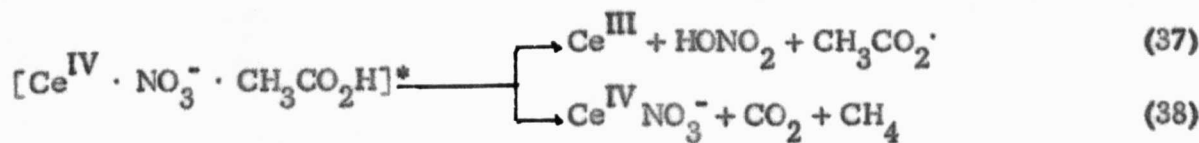
(any H_2O_2 formed from OH^{\cdot} recombination would be oxidised to $\frac{1}{2}\text{O}_2$ by further Ce^{IV}). Martin et al have proposed for a nitrate medium, from results with the flash photolysis⁶⁷ and e.s.r. techniques,⁶⁸ the formation of the nitrate radical as the primary process, i.e.



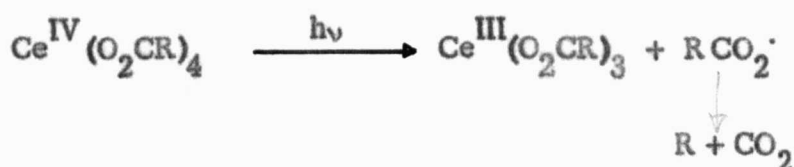
and that subsequent reactions are, in fact, oxidation by NO_3^{\cdot} radical. These authors, continuing their studies with Ce^{IV} ammonium nitrate in glacial acetic acid,⁶⁹ noted a low methane yield, inconsistent with a principal pathway



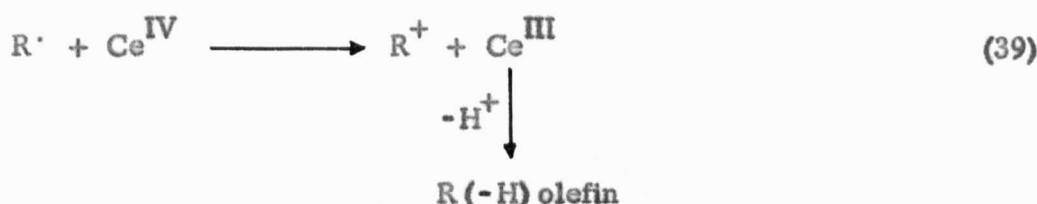
and a photosensitive complex, involving a nitrate ion with a polarised acetic acid molecule coupled to the Ce^{IV} ion (through the carboxyl group) was invoked; electron transfer then takes place on photo-excitation, viz.



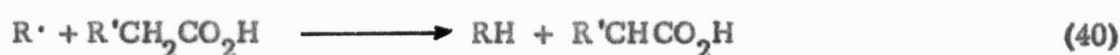
Solutions of Ce^{IV} acetate in aliphatic carboxylic acids are very photosensitive⁵⁷ ($\phi_{\text{Ce}^{\text{IV}}} = -1.17$ for pivalic acid) and decompose on photolysis to give CO_2 and a hydrocarbon, viz. as equation (32),



Radical intermediates are postulated on the grounds of (i) scavenging experiments by Cu^{II} to give products derived from R^+ , and (ii) analysis of the end-products of the reaction. The nature of the hydrocarbons formed is pH-dependent : unsaturated hydrocarbons are formed at low pH via the process



whilst at higher pH, abstraction processes dominate



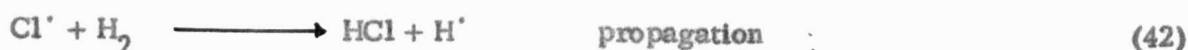
Photolysis of ceric ammonium nitrate adsorbed onto cellulose in the presence of methyl methacrylate produces graft polymerisation⁷⁰ of the latter onto the cellulose.

1.4 Steady State Photochemical Methods

Photochemistry is concerned with the chemical and related physical effects of electronic excitation produced by interaction of electromagnetic radiation with matter. The first law of photochemistry, proposed by Grothaus (1817) and Draper (1843), states that only light absorbed by the system can lead to a photochemical reaction, and the second law, due to Stark and Einstein, states that a molecule absorbs a quantum of light and from the resulting excited molecule arise all the primary processes. These laws lead immediately to the definition of a quantum yield (ϕ) which for any particular process is defined,

$$\phi = \frac{\text{Number of molecules undergoing the particular process}}{\text{Number of quanta absorbed}}$$

From the Stark-Einstein law it can be seen that $\sum \phi$ (primary process) = 1. Product quantum yields can, however, vary from nearly zero to 10^6 . Quantum yields of product considerably greater than one, imply a chain reaction, for example, the quantum yield for HCl production in the photoreaction of hydrogen with chlorine⁷¹ is ca. 10^6 which indicates the following reaction sequence :



(M = a third body)

Quantum yields of much less than one indicate important physical deactivation by collision, fluorescence, internal conversion, intersystem crossing and other processes that lead to no net chemical change. The first requirement for the determination of quantum yields is accurate measurement of the light intensity. This is normally accomplished with the use of a chemical actinometer calibrated previously against some absolute photometric device like a thermopile. Two of the commonest actinometers are those based on uranyl oxalate and ferrioxalate. The uranyl oxalate actinometer,⁷² mentioned earlier (page 6), has a range of applicability between 250 and 450 nm. It depends on the gradual loss of oxalate, with the consequence that the light intensity must be large for reasonable accuracy to be obtained. The ferrioxalate system of Parker,⁷³ which depends on Fe^{II} produced and estimated in the form of its 1:10 phenanthroline complex (λ_{max} 510 nm, $\epsilon = 11,050$), is approximately one hundred times more sensitive and as such can be used with short irradiation times and low light intensities. Measurement of light intensities beyond 450 nm are difficult and a number of new systems have been developed to cope with this. One such system, the Reineckate ion,⁷⁴ i.e. $\text{trans-Cr}(\text{NH}_3)_2(\text{NCS})_4^-$, which depends on production of free NCS^- ion, is sensitive to light of $\lambda > 600$ nm. For studies further into the red (730 nm), the $\text{Cr}(\text{urea})_6^{3+}$ complex has been proposed⁷⁵ as an actinometer.

Complications can occur when the product of the photolysis absorbs the irradiating light; as a consequence, an increasing proportion of the incident light is absorbed by the product as the reaction proceeds. This is the so-called inner filter effect, a conspicuous example of which is the

u.v.-induced transformation of $\text{Fe}^{\text{II}} \text{ aq.}$ to $\text{Fe}^{\text{III}} \text{ aq.}$ ⁷⁶ where the extinction coefficient of the $\text{Fe}^{\text{III}} \text{ aq.}$ produced is several hundred times greater than that of $\text{Fe}^{\text{II}} \text{ aq.}$ If the product is also photosensitive, then this may react to form further products (and, in some cases, produce quantum yields > 1 for loss of reactant) and it is common practice to extrapolate apparent quantum yields to zero time of irradiation. In order to minimise all possible errors, quantum yield experiments are carried out ideally, (i) on solutions that absorb $\sim 100\%$ of all incident light to minimise incomplete absorption, (ii) for only $\sim 1\%$ of the reaction to minimise secondary reactions and (iii) at wavelengths where only the reactant absorbs.

Condition (ii) implies analysis of very small amounts of product with large amounts of reactant. For most volatile products this can be accomplished by v.p.c. and for inorganic metal ions by spectrophotometry. While steady state photochemistry can give us information on quantum yields of reactant disappearance and product formation, the latter give only, at best, an indirect assessment of the primary processes involved.

1.5 Non-Steady State Photochemical Methods

Direct spectroscopic identification of primary processes is difficult, for the species formed are usually radicals, atoms or excited states and the lifetimes of these vary from 10^{-9} to ca. one second. The problems involved then are two-fold; firstly, the species must be produced in a sufficient quantity and in a time that is short compared with their own lifetime and secondly, the rapidity of the detection process must be at least as great as the rate of reaction of the species formed. A number of groups (Porter,⁷⁷ Davidson,⁷⁸ Herzberg⁷⁹) developed the so-called flash photolysis technique. In this a pulse of light of extremely high intensity is passed into the absorbing solutions to produce a large non-equilibrium concentration of intermediates which can be examined by spectroscopic means. A typical assembly is shown in fig. 2(a).

The duration of the flash can be varied by altering the charge on the capacitor () and as a rule the duration is proportional to the square root of the energy; consequently flashes of very short duration normally have very small energies and typical time and energy scales are 1 ms, 10,000 J, $1 \mu\text{s}$, 250 J, 1 ns, 10^{-3} J. Detection of the species formed is either spectrographic or by oscillographic recording. The spectrographic mode

employs a time delay unit which regulates the time between the photolysis flash and the second, analysis flash. The photoelectric mode employs a continuous light source and monitors optical changes at particular wavelengths by means of a monochromator and photomultiplier-oscilloscope apparatus. This detection is adequate for work in the μs time scale.

For work in the nanosecond region, certain modifications are used. The electronic delay unit, reliable on a microsecond scale, becomes erratic and difficult to use. The use of a fluorescent substance as a monitoring source has overcome this difficulty. In this technique part of the photolysis flash is split off from the main beam and used to excite scintillator fluorescence in the monitoring cell which, in turn, is used as the background continuum for the spectrographic recording.

It is clear that for work in the nanosecond region, ordinary flash lamps are inadequate because of the low flash intensity. Lasers using organic dyes as Q-switches form suitable light sources. The commonest lasers in use are ruby (694.3 nm and 347.1 nm if used with a frequency doubling crystal) and neodymium (1060 nm and 503 nm when used with a frequency doubler). Nitrogen lasers have also been utilised ($\lambda = 337.1 \text{ nm}$).⁸¹ With each nanosecond pulse, a number of sub-pulses of picosecond time duration are produced and by choice of a suitable Q-switch, it is possible to produce a train of sub-nanosecond pulses at regular time intervals as well as the main pulse. This so-called mode-locked laser operation has produced some interesting pulse studies on benzophenone singlet lifetime ($\sim 20 \text{ ps}$).⁸² Detection of picosecond pulses can be effected by the two-photo-absorption and fluorescence of azulene in solution.⁸¹

The rotating sector method, utilising short pulses of light at regular intervals of time, has been used in the study of chain reactions and a discussion by Burnett and Melville⁸³ covers most of the theoretical and experimental aspects.

1.6 Matrix Isolation Technique

A versatile approach to the study of reactive intermediates is the matrix isolation technique, whereby the reactive species, once formed, are prevented from further reaction by trapping in an inert solid enabling observation at leisure by u.v., i.r. or e.s.r. spectroscopy. The collision frequency between reactants

can be reduced to a very small value, or zero in some cases, by producing and isolating them in rigid solids at cryogenic temperatures. Early experiments by Lewis et al⁸⁴ in the 1940's showed that the radicals formed from photolysis of frozen aromatic hydrazines could be kept for long periods of time without appreciable decay. Trapping of radicals from the gas phase has since been accomplished⁸⁵ by condensation onto a cold finger after pyrolysis but the most common method is generation within the solid matrix by photolysis or radiolysis. Many systems have been studied in this manner and with the advent of e.s.r. in particular, a large number of primary processes in radiation and photochemistry have been elucidated.

An elegant modification of this technique is the rotating cryostat,⁸⁶ which is a means of mixing two solids together intimately at the molecular level and in a controlled fashion, so that single step chemical reactions occur and the primary products can be preserved for further study; the reaction between sodium and a halohydrocarbon has been extensively utilised, viz.



The principle of this method consists of depositing the two reactants and sometimes an inert solid, as a diluent, from the gas phase, onto a rapidly spinning (ca. 2400 r.p.m.) drum, containing liquid nitrogen, in a high vacuum (10^{-5} torr). Using this technique, a number of interesting radicals have been produced, including $CH_3\dot{C}O$ ⁸⁷ (from CH_3COCl) and $C_6H_5\dot{C}=CH_2$ ⁸⁸ (from $C_6H_5CBr=CH_2$).

1.7 Electron Spin Resonance Method

There are many accounts of the e.s.r. method,⁸⁹ both as regards its theoretical basis and its application to organic,⁹⁰ polymer,⁹¹ transition metal⁹² and photochemistry⁹³ and no comprehensive review need be given here.

1.7.1. Basis of E.S.R.

E.S.R. depends upon the property of spin associated with one or more unpaired electrons. These electrons can interact with (a) the applied magnetic field and (b) other nuclei with spin; the degeneracy of the electron levels is removed and transitions can occur producing the fine and hyperfine structure of paramagnetic ions and radicals. The energy levels may be represented by a number of Hamiltonians which, when combined, form the total Hamiltonian for the spin system.

(i) Interaction of an electron and the applied field can be represented as

$$\mathcal{H}_e = gBS \cdot H \quad (48)$$

where g is the electron spectroscopic splitting factor, S is the spin angular momentum vector, H the applied field and B the Bohr Magneton.

(ii) Although a nucleus with spin I can interact with the magnetic field, these transitions are not observed in the standard e.s.r. experiment.

(iii) Coupling between the electron spin vector and the nuclear spin vector can occur in two ways :

- (a) Fermi contact interaction, which depends only on spin density at the nucleus for interaction to occur and, as such, is isotropic in nature. It may be represented by

$$\mathcal{H}_F = aI \cdot S \quad (49)$$

- (b) Dipole-dipole interaction ; this is proportional to the distance between electron and nucleus and so will be anisotropic in character. However, for a molecule with spherical symmetry, it averages to zero,⁹⁴ and may be neglected except for studies of orientated radicals in single crystals.

Accordingly, the "complete" Hamiltonian for a molecule with spherical symmetry is given by

$$\mathcal{H}_T = gBS \cdot H + aS \cdot I \quad (50)$$

Considering the "high-field" case where both S and I are quantised independently along the direction of the magnetic field, the energy levels become

$$E = gBM_s H + aM_s \cdot M_I \quad (51)$$

where M_s , M_I are the spin quantum numbers for the electron and nucleus respectively and a is the hyperfine coupling constant for the nucleus. For a single unpaired electron, two levels exist, $+\frac{1}{2}gBH$ and $-\frac{1}{2}gBH$; transitions will occur if radiation of energy $h\nu$ equal to the difference in energy between the two states is applied, i.e.

$$h\nu = gBH \quad (52)$$

The spectra of most radicals can be described by equation (51). However, a number of aspects concerning the spectra of organic radicals in the solid state should be mentioned, since a large part of this work deals with organic radicals under these conditions. Details of the spectrometer employed are given in the Experimental Section (page 23)

1.7.2. Linewidth of Radicals in the Solid State

The most striking difference between the spectra of organic radicals in the solid phase and in solution is the linewidth. Linewidths in the solid state may be as broad as 15 Oe, whereas in solution, linewidths of 80 mOe have been reported and it is clear that unequivocal identification of radicals may not be possible in the solid state. The origin of the broadening effect lies with the relaxation processes available to the unpaired electron. The excess population of the ground spin state ($M_s = -\frac{1}{2}$) over that of the upper spin state is about 0.07% at room temperature; absorption of energy, equal to the difference between ground and upper states, in the absence of relaxation processes, would lead to a rapid population of both levels and the absorption of microwave energy would cease. A universal and highly efficient relaxation process in the solid state is spin-lattice relaxation whereby the excess spin energy finds its way into the vibrations and rotations of the surrounding molecules. A direct consequence of this process is the broadening of the absorption lines because of the Heisenberg uncertainty principle. Any mechanism which reduces the lifetime of the spin state causes an uncertainty in the energy content, which means that energy will be absorbed over a range of frequencies, resulting in a finite linewidth; the more efficient the relaxation becomes, the broader the lines will appear. This relaxation process is isotropic, depending only on the efficiency of relaxation for its effect. Another effect which occurs in solids is anisotropic line broadening, which is due to the fixed, random distribution of radicals in the solid state. Because of this, absorption of energy occurs over a range of frequencies and lead to a broad line. In solution, rapid motion of the radical leads to an averaging of this effect and much narrower lines are observed.

1.7.3. Nuclear Hyperfine Interaction

Nuclear hyperfine interaction arises when the radical under study contains nuclei with spin. The electron interacts with the nuclear moments as well as

with the applied field. The spin motion is quantised and the e.s.r. spectrum shows hyperfine splitting into a number of lines, depending on the number of allowed spin orientations. For n equivalent atoms with nuclear spin I , there will be $2nI + 1$ values of M_I corresponding to $2nI + 1$ possible orientations of the nuclear magnetic moment vector with respect to the magnetic field. The selection rules for the transitions are :

- (i) the electron spin change ; $\Delta M_S = \pm 1$
- (ii) the nuclear spin change ; $\Delta M_I = 0$

The selection rule $\Delta M_I = \pm 1$ is an n.m.r. transition and will not be observed under normal e.s.r. experimental conditions. The relative intensities of the lines, i.e. the degeneracy of the hyperfine levels, are given by the coefficients of the binomial expansion of n , for protons, and many examples of this type will be given in later chapters. For a number of non-equivalent protons, the spectrum becomes complex and analysis by computer simulation becomes helpful.

The mechanism of proton hyperfine splitting occurs when unpaired electron spin interacts with the $1s$ orbital of the proton. Assuming that the unpaired electron of the organic radical is in a px orbital, it is difficult at first to account for any hyperfine interaction because the interacting protons normally lie in a nodal plane of zero spin density. Numerous theoretical attempts have been made to explain this phenomenon, including zero point vibrations⁹⁵ of the protons and indirect coupling through the chemical bond.⁹⁶ By far the most successful is the sigma- π configuration interaction approach of McConnell.⁹⁷ A direct consequence of this is the relationship between the proton splitting constant and the unpaired spin density at the associated carbon atom, viz.

$$a_{CH}^H = Q_{CH}^H \rho_C \quad (53)$$

Q_{CH}^H is a measure of the sigma- π interaction and is called the McConnell constant. McLachlan,⁹⁸ using a valence bond treatment, arrived at a similar result to account for methyl group splittings, i.e.

$$a_{CH_3}^H = Q_{CCH_3}^H \rho_C \quad (54)$$

The theory has been developed further by Karplus and Fraenkel⁹⁹ to account

for ^{13}C atom splittings as well as ^{14}N splittings.

1.7.4. Alkyl Radicals in the Solid State

The solid-state spectra of alkyl radicals are characterised by their large proton splittings (ca. 20 Oe) and relatively simple hyperfine pattern. The large splittings come from two sources :

(i) α - H splittings ; this is a direct result of the large spin density on the α - C atom because there is no pi-system to delocalise the electron and reduce the spin density on each carbon atom.

(ii) β - H splittings are large because the β - protons lie in a plane parallel to the $2p_{\pi}$ orbital of the unpaired electron (c.f. aromatic species where they lie in the nodal plane) and polarisation of the C - H bond is greater (see diagram 2(b)). However, this means that the degree of polarisation, and hence the splitting, is dependent on the angle between the C - H bond and the $2p_{\pi}$ orbital (see diagram). It is known that, for certain radicals locked in a particular con-figuration, the β - protons show different splittings, e.g. $\text{CH}_3\text{CH}_2\text{CH}_2$ at 77°K^{100} shows two inequivalent β - proton splittings (one of 46 Oe and the other of 24 Oe). The angular dependence is incorporated into the McConnell relationship,

$$a^{\text{H}} = Q_{\text{CCH}}^{\text{H}} \rho_{\text{C}} \cos^2 \theta \quad (55)$$

which, for a system in which the β - protons are free to rotate about the C - C bond, reduces to

$$\begin{aligned} a^{\text{H}} &= Q_{\text{CCH}}^{\text{H}} \rho_{\text{C}} \frac{1}{2\pi} \int_0^{2\pi} \cos^2 \theta \, d\theta \\ &= \frac{1}{2} Q_{\text{CCH}}^{\text{H}} \rho_{\text{C}} \end{aligned} \quad (56)$$

An empirical relationship has been developed to account for this angular dependence

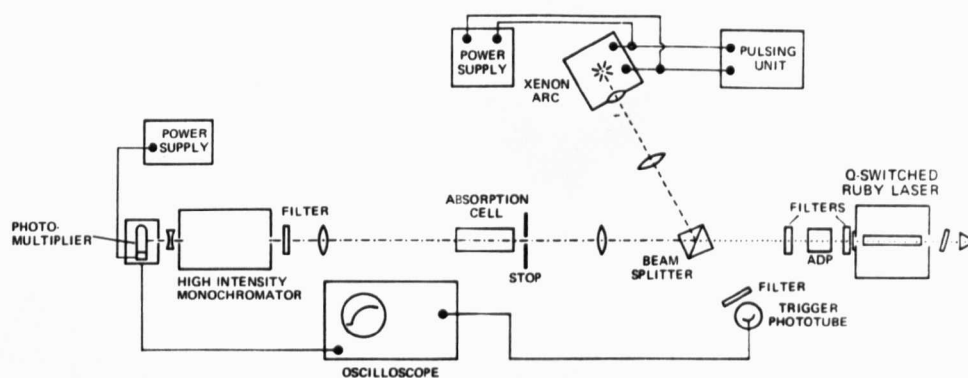
$$a_{\text{B}}^{\text{H}} = B_1 + B_2 \cos^2 \theta \quad (57)$$

where $B_1 = 4$ Oe and $B_2 = 50$ Oe approximately. It is clear that there is no efficient way of introducing unpaired spin to the γ - protons because the overlap between the γ 1s proton orbital and the α - carbon $2p_{\pi}$ orbital is small.

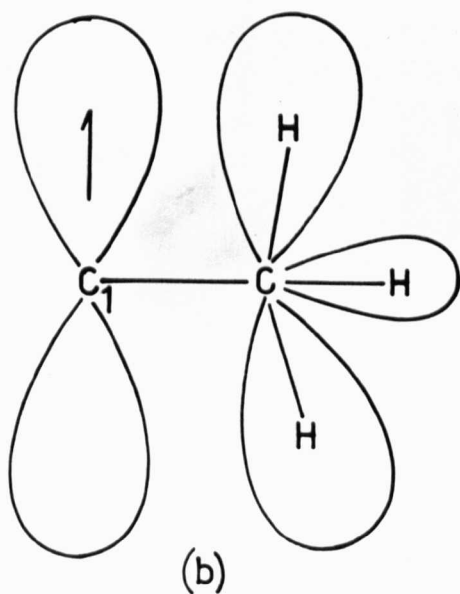
Calculations¹⁰¹ on these small splittings have borne this out. Because of the large splittings involved, it is possible to analyse alkyl radical spectra in the solid state whilst line broadening tends to obscure the smaller splittings of aromatic species.

FIGURE 2

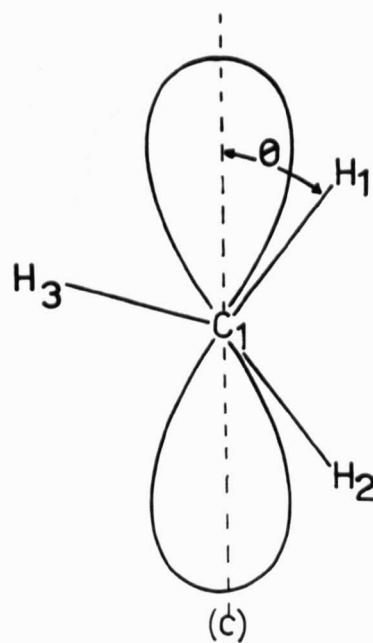
- (a) Schematic diagram of a laser flash-photolysis apparatus
- (b) Overlap of electronic orbitals in a C-CH₃ fragment
- (c) The effect of dihedral angle ϕ on overlap of electronic orbitals in a C-CH₃ fragment (looking down the C₁-C bond axis)



(a)



(b)



(c)

1.7.5. g-Values

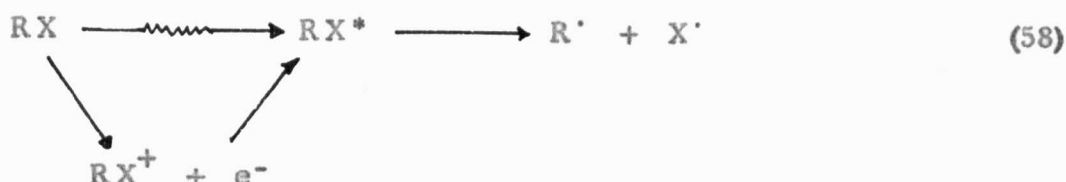
The e.s.r. resonance condition (equation 52)

$$h\nu = gBH$$

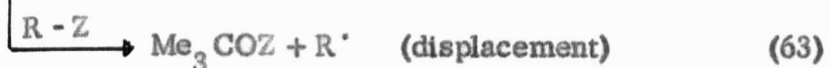
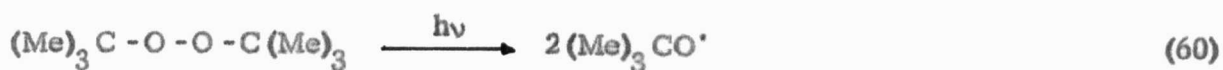
relating frequency (ν) to magnetic field strength (H) contains a dimensionless quantity, g , which is referred to as the g -factor for a particular system. g -Factors are essentially a measure of the coupling between electron spin and ^{orbital} nuclear angular momentum. In the case of most organic free radicals, the energy separation between angular momentum levels is large and hence, only the lowest level is filled and the g -factor corresponds closely to the free spin value of 2.00232. Variations of the g -value are observed in the solid state where there is no time-averaging effect of the g -tensor by rapid motion. For radicals with a symmetric g -tensor, two g -factors will be observed, one caused by components of the g -tensor lying parallel to the field (g_{\parallel}) and the other caused by components at right angles to it (g_{\perp}). For asymmetric g -tensors, three values are observed (g_x, g_y, g_z). Theoretical studies¹⁰² on line shapes have been carried out and use will be made of them in the analysis of certain spectra. Measurement of these parameters is an indication of the type of radical present and is of utmost importance in identifying radicals with little or no hyperfine structure.

1.8. Application of the E.S.R. Technique to Reaction Mechanisms

Initially, applications of the e.s.r. technique to reaction mechanisms concerned mainly the processes involved in radiolysis and photolysis of compounds in both crystalline and frozen solutions at cryogenic temperatures. Methyl and ethyl radicals were detected after radiolysis of methane and ethane at 77°K,¹⁰³ but spectra from higher hydrocarbons were complex due to the production of more than one radical. Ayscough and Thomson¹⁰⁴ avoided this problem by γ -irradiating a series of solid alkyl halides, viz.



They were able to measure α - and β -proton splittings in a number of alkyl radicals. The production of alkyl radicals, in liquid hydrocarbons at low temperatures by Fessenden and Schuler,¹⁰⁵ using continuous irradiation with 2.8 Mev electrons, enabled the small γ -protons and second order splittings¹⁰⁶ to be resolved. This method also provided absolute second order rate constants for radical disappearance. It has since been developed to include radiolysis of aqueous systems, and by the use of selective scavengers, the reactions of $\cdot\text{OH}$,¹⁰⁷ H^\cdot ,¹⁰⁸ and e_{solv}^- ¹⁰⁹ have been studied. Reactions of the oxidising species generated from the reaction between Ti^{III} and H_2O_2 ¹¹⁰ in a rapid-flow system have been characterised, including its abstraction from $\text{C}-\text{H}$ ¹¹¹ bonds and its addition to $\text{C}=\text{C}$ ¹¹² bonds. The use of the couples $\text{Ti}^{\text{III}}/\text{NH}_2\text{OH}$,¹¹³ $\text{Ti}^{\text{III}}/\text{H}_2\text{O}_2/\text{HCO}_2\text{H}$ ¹¹⁴ and $\text{Ti}^{\text{III}}/\text{S}_2\text{O}_8^{2-}$ ¹¹⁵ enables reactions of NH_2^\cdot , CO_2^\cdot and HCO_2^\cdot and SO_4^\cdot respectively to be followed. The rapid-flow technique has also been used with Ce^{IV} and phenols to produce aryoxyl radicals;⁶² again, solutions of e_{solv}^- in liquid ammonia have been used to elucidate the mechanism of reduction of aromatic halides,¹¹⁶ carboxylic acids¹¹⁷ and styrenes,¹¹⁸ and conformational changes in cyclohexen-2-one radical-anion¹¹⁹ systems. The use of e.s.r. in the study of photolytic processes has long been established in the solid state. Livingston and Zeldes have extended the application to a study of liquids during photolysis, using an intense source (analogous to the continuous irradiation method of Fessenden and Schuler) and have examined solutions of alcohols and hydrogen peroxide,¹²⁰ acetone,¹²¹ aliphatic nitro-anions¹²² and electron donor-acceptor reactions with oxalic acid.¹²³ Kochi and Krusic¹²⁴ have extended previous work of Adams¹²⁵ concerning reactions of the tertiary butoxy radical, produced from photolysis of di-tert-butyl peroxide.



They have examined a number of structural problems including homoallylic rearrangements of cyclopropylcarbonyl¹²⁶ radicals, the structure of the non-classical 7-norbornenyl¹²⁷ radical and hindered rotation in alkyl radicals.¹²⁸ In a similar series of experiments by Hudson et al,¹²⁹ an alternating line-width effect in $^\cdot\text{CH}_2\text{OH}$ was noted and the energy of rotation of the -OH group calculated; therefrom further work by this group covers radicals containing Si, Ge, B, Sn and P.¹³⁰ Symons et al¹³¹ have made a very extensive study of the e.s.r. spectra of inorganic radicals, usually formed from γ -irradiation of the parent ion.

1.9 Purpose of this Work

The study of primary processes in photo-oxidations of organic substrates by metal ions has almost invariably been accomplished without direct spectroscopic examination of the primary products, incorporating instead classical methods such as end product analysis, radical scavenging and quantum yield measurements of both products and reactants (sections 1.2 - 1.4). The purpose of this work is to examine by e.s.r. spectroscopy the primary species formed during photo-oxidation by metal ions of a wide variety of organic substrates and stabilised in the solid state at 77°K. The secondary reactions are studied by warming the sample and allowing the radicals to diffuse and react. The logical extension of the work to the liquid phase has also been achieved, enabling highly resolved radical spectra to be observed. The metal ions chosen were :

- (i) Ce^{IV} , known to be a powerful one-electron oxidant and producing charge-transfer complexes in solution with the substrates of interest. Photolysis in the corresponding C - T band is shown here to effect electron transfer. The thermal chemistry of Ce^{IV}

is well-documented (section 1.3) and comparisons between thermal and photochemical oxidations are made.

- (ii) U^{VI} ; whilst the photochemistry of U^{VI} in the presence of reducing organic and inorganic species is well known, the primary processes are not at all clear (see section 1.2). It was contemplated that with the aid of the cryogenic e.s.r. technique, it would be possible to establish some of these processes and compare them with similar reactions of Ce^{IV} and some other metal ions.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2. EXPERIMENTAL TECHNIQUES

2.1 The E.S.R. Spectrometer and Accessories

The e.s.r. spectrometer used in this work was a conventional X -band instrument (Decca Radar Ltd., model X - 1), employing 100 kc/s modulation of the magnetic field. After phase detection and amplification, the resultant signal appears in its first derivative form. A general purpose cavity, operating in a TE 102 mode, with two tuning controls and one coupling control, was fitted as standard. The original copper-plated glass windows of the cavity were replaced by the more robust gold-plated ceramic variety. Photolysis of samples was carried out through two slots machined in the front of the cavity. For studies at cryogenic temperatures, the cavity was fitted with a variable temperature insert (Decca Radar Ltd.) which allowed a controlled flow of cold nitrogen gas to pass over the sample tube. The temperature was maintained with a platinum resistance thermometer and a feedback circuit to a heating element in the cold nitrogen gas flow. In this manner the temperature could be controlled to $\pm 0.5^{\circ}\text{C}$. Sometimes a Spectrosil tail dewar vessel (constructed by Mr. K. Holden of the departmental workshop) containing liquid nitrogen, was employed for studies at 77°K . The magnet system was a seven-inch electromagnet (Newport Instruments Ltd.) with a maximum field of 6000 Oe. However, since the radicals under observation had a g-value close to that of the free spin value, a field of ca. 3300 Oe was normally used. In order to observe the resonance, a small portion of the magnetic field (up to 600 Oe), around $g = 2$, was swept by a mechanical generator and slow sweep unit. Typically, sweep times were ca. 1000 secs. and the signal was fed to two chart recorders, a Smiths "Servoscribe" X - t recorder and a Hewlett Packard X - Y recorder. Sweep times and field modulation amplitude were adjusted to give maximum resolution. Saturation effects (caused by high microwave power) were not noted in the solid state due to efficient spin relaxation processes.

2.2 Measurement of Splitting Constants and g-Values

Calibration of the magnetic field was accomplished using a dilute alkaline

solution of Fremy's salt (potassium peroxyamine disulphonate). The dianion radical, $\cdot\text{NO}(\text{SO}_3)_2^{2-}$, exhibits three lines of equal intensity with a splitting of 13.07 Oe. Measurements were always carried out on the same day as samples were run and the average of a number of scans was taken. Measurements of the magnetic field strength were effected with the aid of a proton resonance probe (Decca Radar Ltd.). This probe could be set at any particular field value and was connected via a relay to an interval marker on the X - t recorder and the remote pen drop control on the X - Y recorder. In practice, the probe was set and then calibrated using the klystron frequency (9270.3870 mc/s) against Fremy's salt ($g = 2.0055$), to allow for any disparity between the sample and probe positions in the magnetic field. Field values could be measured to ± 0.1 Oe using this technique and g -values were taken as the average of a number of different scans.

2.3 Analysis and Computer Simulation of Spectra

Analysis of the spectra produced was sometimes difficult due to line broadening effects, which obscured some of the smaller splittings. The use of a computer program (ESRTEST) greatly improved the accuracy of analysis of spectra. The program which calculates line positions and intensities applies a Lorentzian or Gaussian line shape to produce the required spectrum. It was found that, for most radicals in the solid state, simulation was possible using broad Lorentzian lines with linewidths in the region 2 - 10 Oe. A second program (ESRTT2) was used to simulate spectra due to a mixture of radicals. Listings of both these programs appear in the appendix. This simulation procedure was only effective for isotropic splittings. When anisotropic effects were encountered, use was made of the work by Kneubühl and others¹⁰² who computed spectra of radicals showing anisotropy of both g and A (hyperfine splitting) tensors.

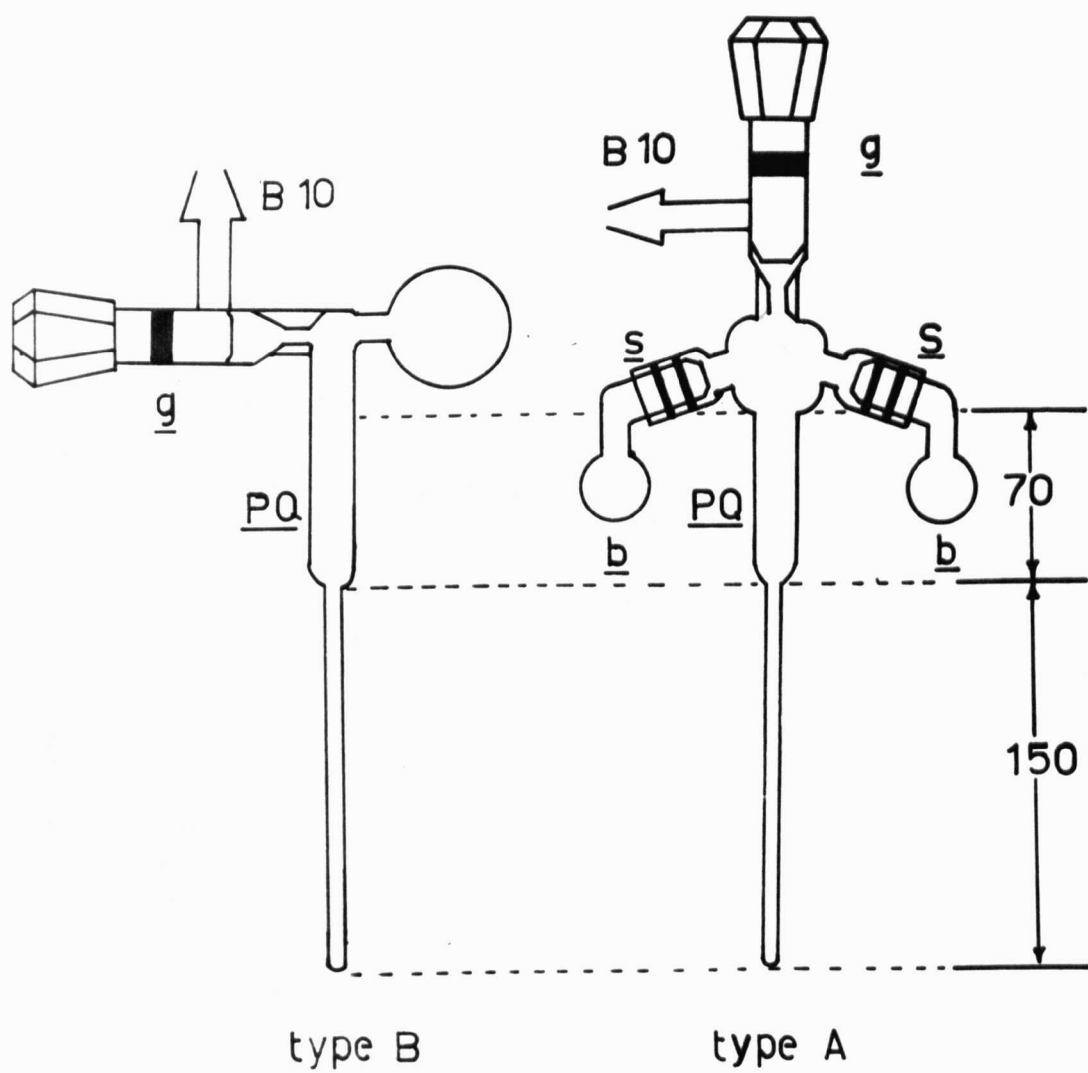
2.4 Cells for Solid State Work

It was necessary to devise a sample cell that was robust, free from grease and other radical scavengers and able to maintain a high vacuum, and a typical cell is shown in fig. 3. The sample tube of Spectrosil (Thermal Syndicates Ltd., 3.2 mm o.d.) was joined to a quartz tube (10 mm o.d.) and thence via a graded seal (pq) to a Pyrex tube. 0.5 ml each of solutions of

FIGURE 3

Cells for Solid-State Studies

**(the B10 cone is normally at
right angles to the plane of the paper)**



metal ion and substrate were placed separately in the bulbs (b) which were then placed in the sidearms (s) fitted with Teflon O-rings, each backed by an O-ring of Viton A. The upper section was constructed from thick-walled Pyrex to enable the device to withstand considerable torque, and a B10 cone provided the connection to a high vacuum line. The vacuum was maintained by a greaseless stopcock (g), again based on a Teflon key, in a precision bore Pyrex tube, backed by three Viton A O-rings, constructed initially by Mr. K. Holden of the departmental workshop. Later models used commercial stopcocks of Quickfit and Quartz Ltd. ("Rotoflo" model) and J. Young Ltd. of Acton, but these were found to be less robust than the departmental variety, the "Rotoflo" tap having a poor backing seal and Young's model being prone to cracking. The solutions were degassed by a series of freeze-pump-thaw cycles, the stopcock closed and the sample removed from the vacuum line. Following melting of the solutions, mixing was effected by inversion and vigorous shaking (sometimes, particularly with alcoholic solutions, a red or orange colour developed), and a portion of the mixed solution immediately shaken into the e.s.r. tube and frozen to 77°K , being then ready for photolysis. For samples consisting of metal ion salts dissolved in neat organic solvents, the cell shown in fig.3b was used, consisting of a single bulb and a Spectrosil sample tube, degassing being effected as before.

2.5 Light Sources

Initial experiments were conducted with a medium pressure mercury lamp (Hanovia 250 watt) and photolysis of samples for ca. 30 minutes in a quartz dewar at 77°K , followed by transfer to the e.s.r. cavity and subsequent examination at 77°K showed that electron transfer does indeed occur upon photolysis of metal ions in solution at 77°K . The medium pressure lamp has a number of disadvantages :

- (i) it has a low light intensity between 300 - 350 nm where the metal complexes absorb,
- (ii) it is large (ca. 10 cm) and difficult to focus efficiently.

These factors necessitate long periods of sample irradiation in order to build up an observable quantity of radicals. Such problems were overcome

FIGURE 4

Irradiation Facilities

(all dimensions are in millimetres)

(a) 100 watt Mercury Arc

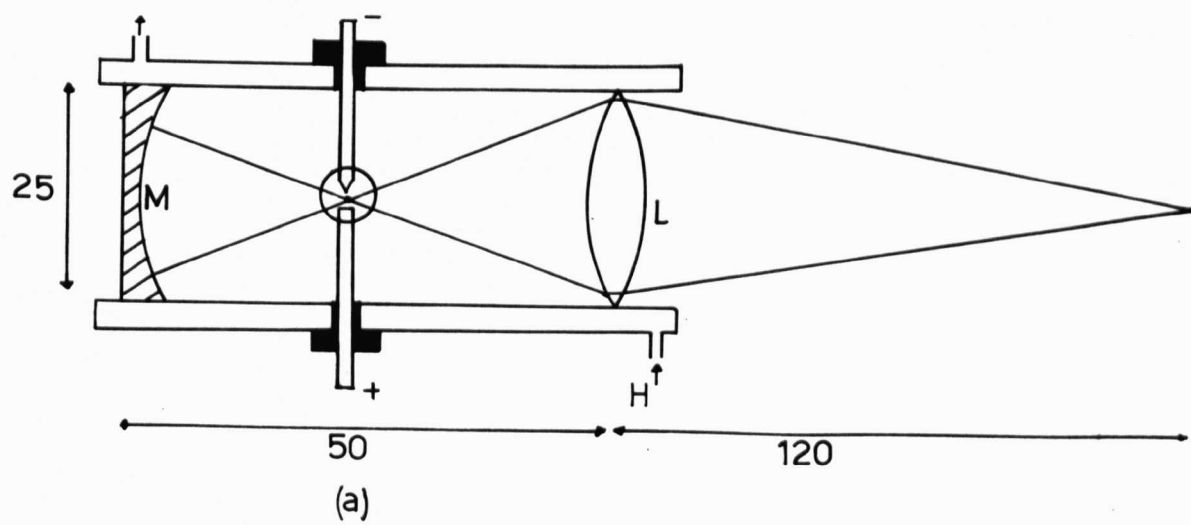
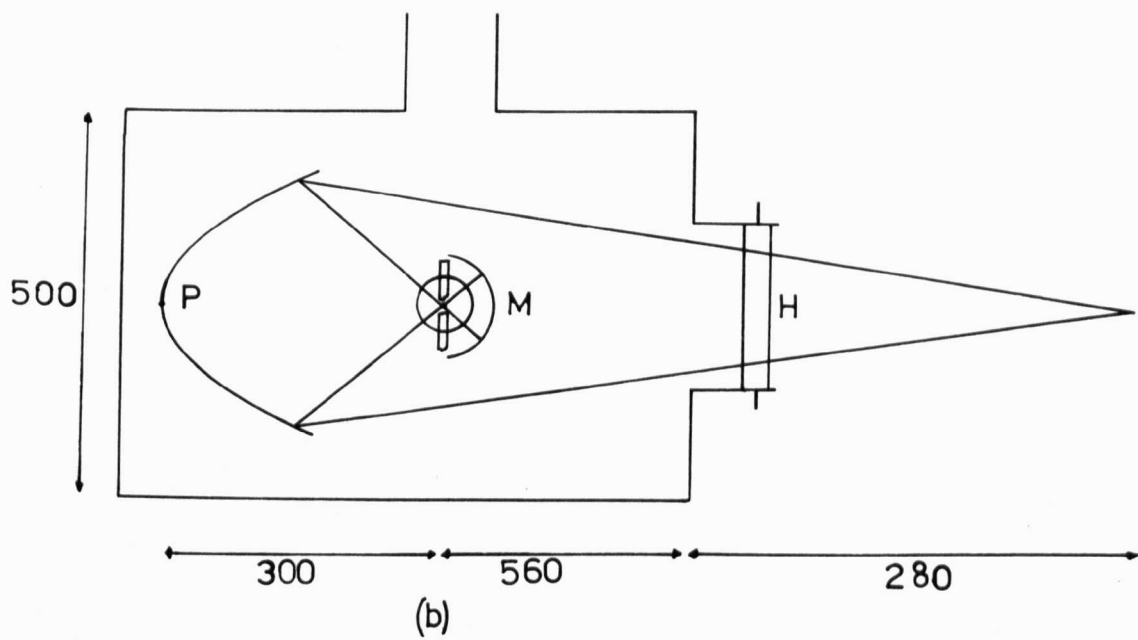
(b) 1 Kw Xe High Pressure Arc

H - Heat Filter

L - Spectrosil Lens (12 cm focal length)

M - Spherical Mirror

P - Parabolic Mirror



with the aid of a high pressure mercury compact arc lamp (Hanovia 100 watt) fitted with a reflector and a lens (fig. 4a) to focus the beam to a sharp spot of ca. 1 cm diameter. Heat dissipated from the arc lamp is removed from the system by a water cooled jacket and the production of ozone resulting from short wavelength u.v. passing through the atmosphere, is obviated by flushing the interior of the lamp housing with nitrogen. The mercury arc produces a continuum and half of the light energy appears in the 290 - 360 nm region, although the system will produce and transmit to wavelengths as low as 185 nm. Using this apparatus, photolysis times were reduced to ca. 1 - 10 minutes, depending on the crystallinity of the sample. The extension of the work to study photo-oxidations in the liquid phase required a much greater light flux than in the solid state and consequently, a 1000 watt Xenon point-source fitted with reflectors to focus the light to a sharp spot ca. 2 cm diameter, was employed (fig. 4b). The lamp was designed by R. Wilson of the National Physical Laboratories and constructed by Mr. H. Gurnham in the University of Warwick workshop. Focussing was achieved by rack and pinion mechanisms which enabled the mirrors to be moved horizontally and vertically. A water-cooled heat filter with Spectrosil windows and sometimes an OX 7 filter was used to reduce effects due to sample heating in the cavity. Cooling of the lamp mirrors was accomplished by a small auxiliary fan inside the lamp housing, while ozone was removed through a flexible tube (six inch diameter) to a fume extract. Similar high intensity lamps have been used by Livingston and Zeldes¹²⁰ and Kochi et al¹²⁴ who utilised a quartz lens to focus the beam instead of a parabolic mirror.

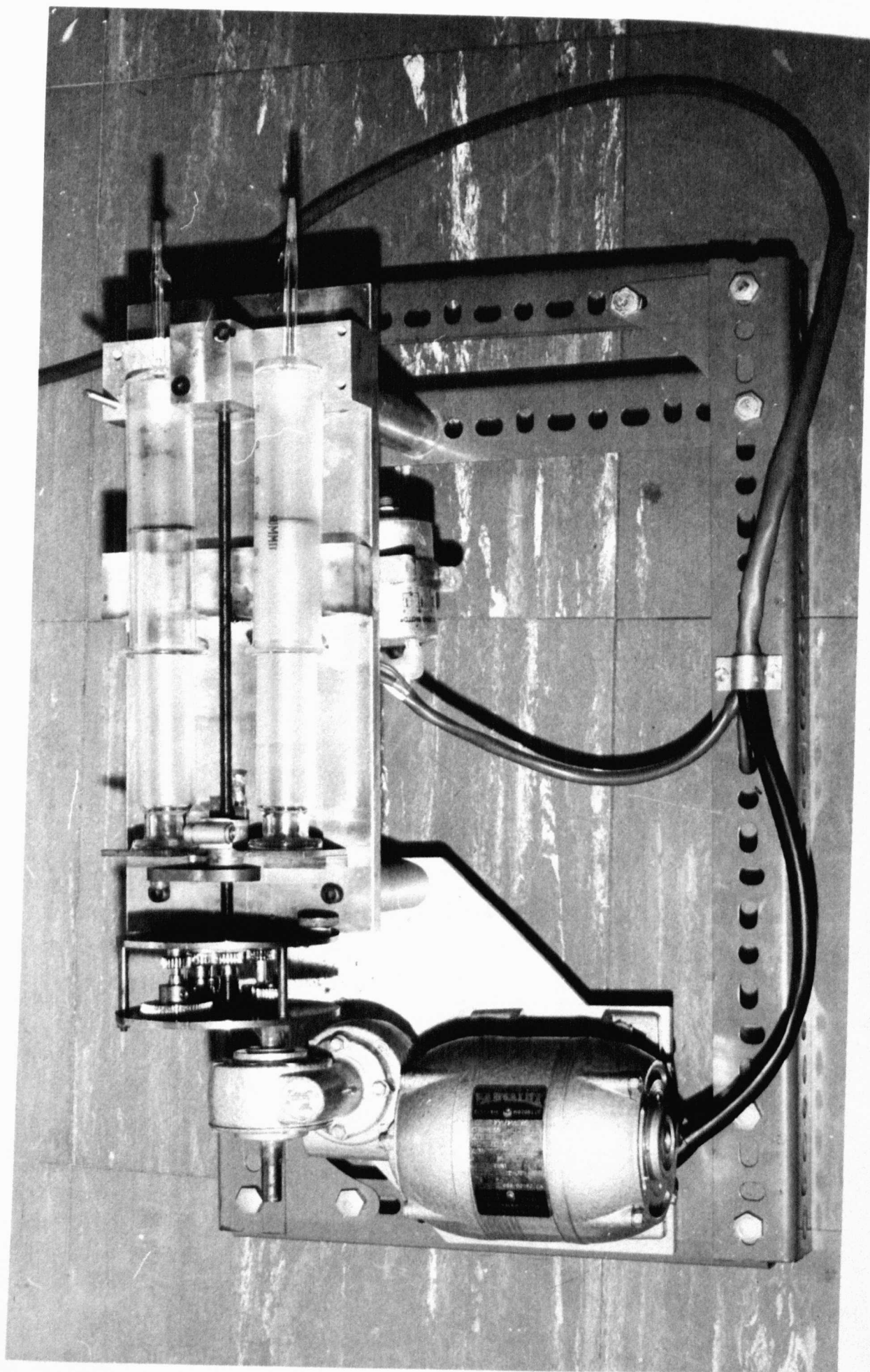
2.6 Filters

A number of filters were employed to enable photolysis over a range of wavelengths to be carried out.

- (a) OX 7 filter (Chance glass). This filter had > 95% transmission from 230 - 405 nm, and was used as a heat filter to remove long wavelength radiation which caused excessive heating of the cavity at very slow flow rates.
- (b) Corning clear glass 50.54. This had > 95% transmission for all wavelengths > 305 nm and was used

FIGURE 5

Syringe Drive Unit



to prevent direct photolysis of the organic substrates, some of which absorbed strongly below 300 nm.

- (c) Corning clear glass C.50.52. This had > 95% transmission for all wavelengths > 360 nm.

2.7 Low Temperature Flow System

The study of liquid phase photolysis of metal ions necessitates the development of a flow system to build up a sufficient concentration of radicals for observation. It is also advantageous if the rate of radical-radical and radical-metal ion reactions can be reduced. This is achieved by a low temperature flow method. Some of the problems associated with low temperature flow systems have been mentioned by Livingston and Zeldes¹²⁰ (viscosity of solutions and poor temperature control) and it is necessary to depart from the conventional gas powered flow apparatus. The problems were overcome by using a mechanical syringe drive (fig. 5). The electric motor (Parvalux 5 r.p.m. 35 lb/ins) was connected to the syringe drive through a planet-type gearbox giving four output speeds. By a suitable choice of both output gear and syringe size, flow rates from 0.5 ml/min to 15 ml/min could be obtained. The two syringes were connected via capillary glass tubing and greaseless ball and socket joints (to allow some degree of flexibility in the system) to a small mixer, based on the design of Dixon and Norman¹¹⁰ situated at the bottom of the flow cell (fig. 6(b)(c)). A number of cells with varying optical path lengths were employed, up to 2 mm. The thickest cell that did not give excessive microwave losses for the particular sample being studied was used. Temperature control was effected by passing cold nitrogen gas through the sample cell. This, in effect, cooled the liquid slowly passing up the cell, and at the same time prevented condensation within the cavity by blowing out of the cell and into the cavity (fig. 6(b)). The cell fitted into a modified variable temperature insert and utilised the Decca Radar temperature controller described earlier. The temperature of the flowing solutions was measured with an electric thermometer (Comark Ltd). Using this apparatus it was possible to study reactions at temperatures as low as 140°K.

2.7.1. Preparation of Solutions for Examination in the Liquid Phase

Solutions must be free from oxygen and the apparatus shown in fig. 6(a) was used. Nitrogen from a cylinder was passed through the U-tube which

FIGURE 6

Flow System Accessories

(a) Degassing Unit

(b) Flow Cell

B - Main Bubbler

P - Prebubbler

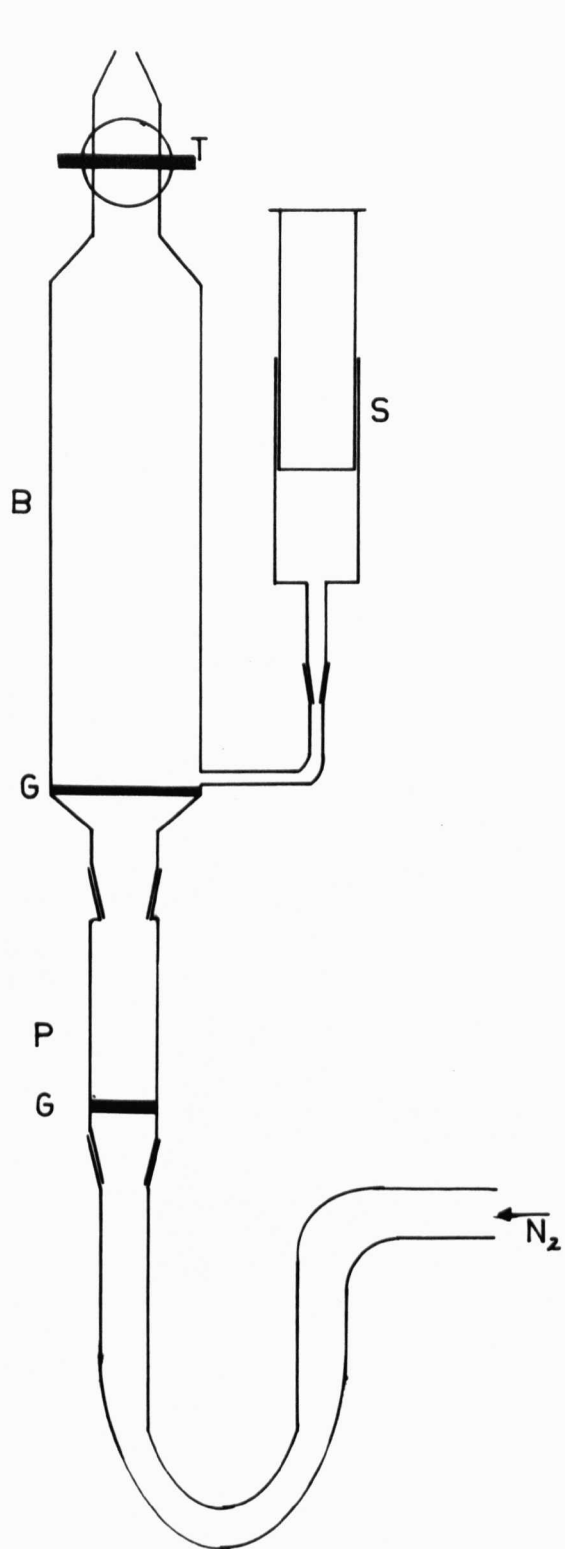
G - Glass Sinters

S - Syringe

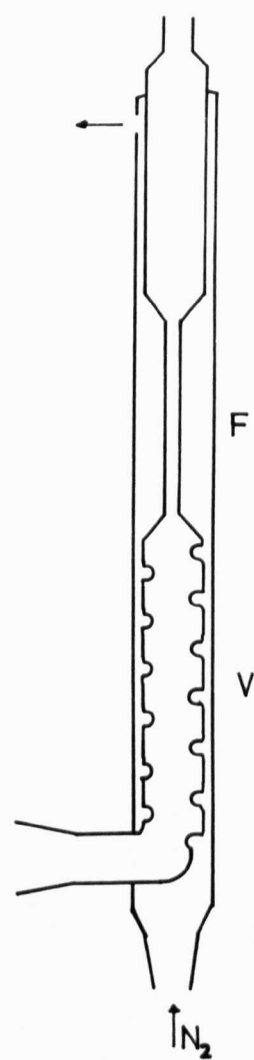
V - Indented Cooling Column

F - Flat Cell Windows

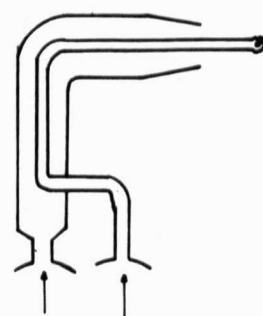
(c) Mixer to fit Flow Cell



(a)



(b)



(c)

contained glass wool to trap any solid impurities, and escaped eventually through the tap T. The prebubbler P contained a few ml of the solution to be degassed, and the remainder of the solution (up to 60 ml) placed in the main bubbler B. The prebubbler saturated the nitrogen with vapour to compensate for loss of volatile material from the main bubbler in the nitrogen stream. While the nitrogen was displacing the air from the solution, tap T was closed and the solution forced into the syringe, causing the barrel to rise. The tap was opened, allowing the barrel to fall and ensuring that solution in the side arm was also thoroughly degassed. After approximately twenty minutes bubbling, T was closed and the syringe allowed to fill completely. T was then opened and the syringe removed and capped with a sealed-off B5 socket, taking care not to trap any small air bubbles. Three main sizes of syringes were used; 50 ml, 30 ml (Summit syringes) and 10 ml (constructed in the departmental workshop) and all were fitted with a B5 capillary cone. Later bubblers had a greaseless tap fitted between the main bubbler and the syringe to facilitate filling two syringes with the same solution, particularly in the case of uranyl systems, where the oxidant was dissolved in neat substrate. The syringes were placed in the flow system, and the motor switched on, when the desired flow rate and temperature were attained, i.e. the lowest temperature possible without the solvent actually freezing, the cavity was tuned and then the sample was photolysed. The flow rate was then readjusted to give maximum signal intensity if necessary.

CHAPTER 3

Ce^{IV} PHOTO-OXIDATION OF ALCOHOLS

3. Ce^{IV} PHOTO-OXIDATION OF ALCOHOLS

3.1 Introduction

Ce^{IV} and alcohols are known to form C-T complexes identified from the red-shift in the absorption spectrum when solutions of Ce^{IV} and alcohols are mixed (page 7). Photolysis in this band leads to electron transfer and the products are stabilised by matrix isolation at cryogenic temperatures. This chapter deals with the primary processes in the photo-oxidation of a large number of alcohols.

In order to standardise the experiments, five methods of sample preparation were employed and will be referred to in the next three chapters of this work.

Method A - ceric perchlorate (0.1 M) in aqueous 4 M HClO_4 and the organic substrate (up to 1 M) in water. These samples were prepared and degassed in a sample tube type A.

Method B - (used only when the substrate was insufficiently water-soluble to give a solution concentration > 0.05 M) a small quantity of spectroscopic grade acetonitrile was added. This method was only used sparingly due to production of CH_2CN radical from Ce^{IV} perchlorate oxidation of acetonitrile, which obscured some of the substrate-radical spectrum.

Method C - ceric ammonium nitrate dissolved in neat organic liquid to ca. 0.1 M or saturation (whichever was the least concentrated). Samples were prepared in this way in tube type B.

Method D - ceric ammonium nitrate (0.1 M) and the organic substrate (up to 1 M) in water.

Method E - as for D but with sufficient spectroscopic grade acetonitrile to produce a homogeneous system.

3.2 Results

3.2.1. No Added Substrate

(i) Ceric Perchlorate. - Using filtered light (Corning 50.54, $\lambda > 300$ nm) a weak H^\bullet signal was obtained ($a_{\text{H}} = 504$ Oe), which intensified on removal of the filter. When CH_3CN was added as a co-solvent, signals due to CH_2CN

were observed, from photo-oxidation by Ce^{IV} .

(ii) **Ceric Ammonium Nitrate** - A 1 M aqueous solution produced a very weak signal around $g = 2$ before photolysis and a small signal assigned to NO_2 (see discussion) with filtered light. A larger NO_2 and H-atom signals were detected on removal of the filter. Solutions of ceric ammonium nitrate in CH_3CN produced no absorption on photolysis $\lambda > 300 \text{ nm}$ and only a small NO_2 absorption on removal of the filter.

3.2.2. Primary Aliphatic Alcohols

Methanol - Methods A, C and D all produced a distorted but reproducible basic 1 : 2 : 1 triplet of average separation $20 \pm 2 \text{ Oe}$ (figures 7 (a), (b)); methods C and D produced, in addition, two wing peaks of average separation $102 \pm 2 \text{ Oe}$, the high field peak being of asymmetric character (fig. 7 (b)). These wing peaks were a feature of all experiments involving ceric ammonium nitrate irrespective of substrate, though in a number of cases, e.g. the tertiary alcohols and later the aldehydes, its intensity was only a few percent. of that of the co-existing carbon radical. This spectrum was attributed to the NO_2 radical for reasons given later. The 1 : 2 : 1 triplet, although distorted probably through anisotropy effects, compared with the spectra obtained with higher aliphatic alcohols, is probably due to CH_2OH , which has been characterised in rigid solution by photolysis¹³¹ and radiolysis methods¹³² ($a_{\text{H}} = 19 \text{ Oe}$). Its solution spectrum obtained by oxidation with the $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ couple¹¹⁰ and by photolysis of liquid methanol containing H_2O_2 ¹²⁰ shows a principal proton coupling constant of 17.2 Oe at room temperature and 17.83 at 223°K.

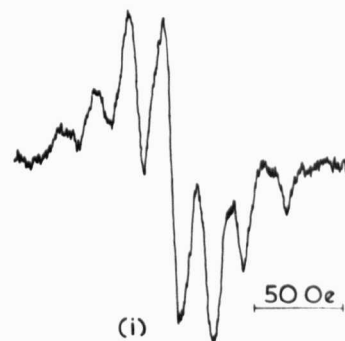
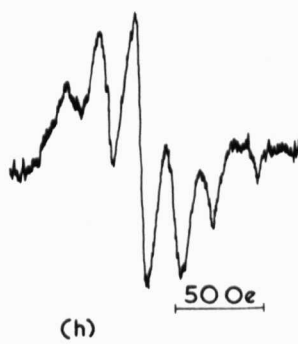
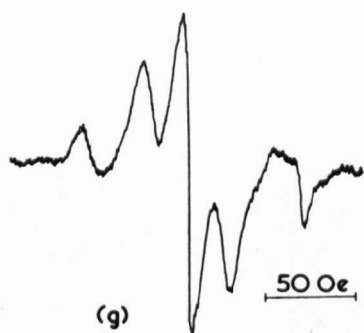
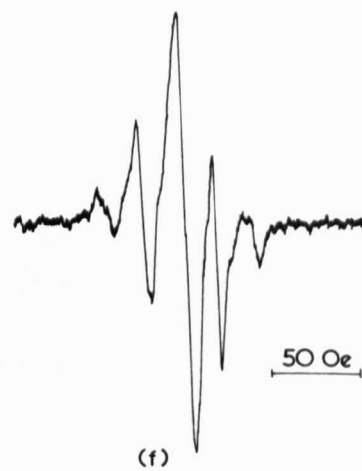
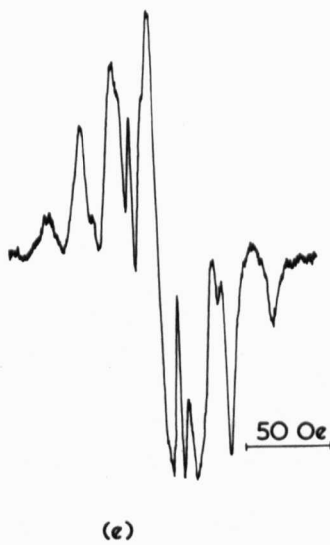
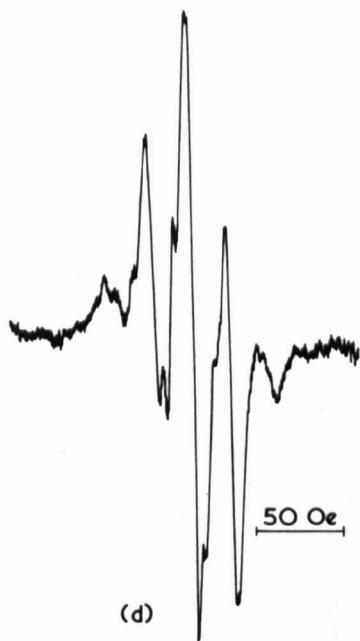
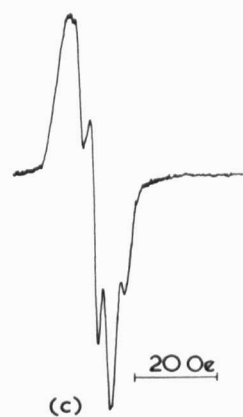
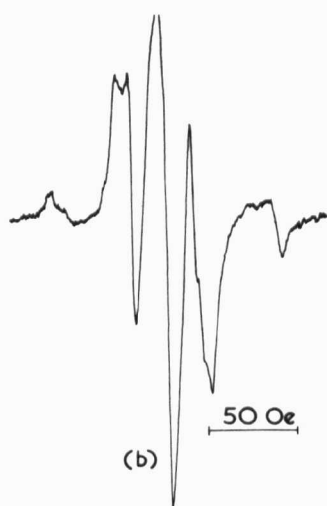
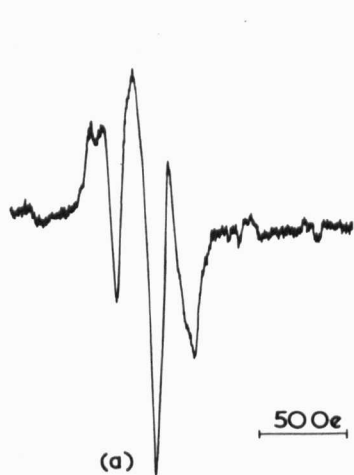
Methanol-d⁴ - The spectrum obtained by method C and shown in figure 7 (c) is much narrower than that obtained from methanol and suggests formation of a poorly resolved CD_2OD spectrum. The high field half of the spectrum was analysed in terms of two equivalent deuterium atoms with a splitting of 3.2 Oe which is in good agreement with the theoretical value of 2.7 Oe calculated from the ratio of the nuclear magnetic moments of H to D (6.5 : 1) and hence the ratio of the splittings. Radiolysis of CD_3OH produced only a broad unresolved singlet.¹³²

Ethanol - Methods A and C produced a basic five-line binomial spectrum of average separation $22.3 \pm 0.1 \text{ Oe}$ with additional subsidiary peaks of separation

FIGURE 7

**E.S.R. Spectrum Obtained During Photo-Oxidation of
Primary Alcohols by Ce^{IV}**

- (a) Methanol (Method A)
- (b) Methanol (Method C)
- (c) Methanol- d^3 (Method C)
- (d) Ethanol (Method A)
- (e) Propan-1-ol (Method D, 77°K)
- (f) Propan-1-ol (Method D warmed to $\sim 175^\circ\text{K}$)
- (g) 2-Methylpropan-1-ol (Method C)
- (h) Butan-1-ol (Method C)
- (i) Pentan-1-ol (Method C)



22.7 Oe probably due to $\text{CH}_3\cdot$. The spectrum shown in figure 7 (d) is that obtained by method A. The five-line spectrum closely resembles that obtained on photolysing ethanol and H_2O_2 at low temperatures¹³¹ and on radiolysis of ethanol at 77°K¹³² ($a_{\text{H}} = 22$ Oe by both methods) and is assigned to $\text{CH}_3\dot{\text{C}}\text{HOH}$. The solution spectrum of $\text{CH}_3\dot{\text{C}}\text{HOH}$ produced by photolysis of ethanol and H_2O_2 ¹²⁰ shows $a_{\text{CH}_3} = 22.14$, $a_{\text{CH}} = 15.24$. The apparent equivalence of all the protons in the solid state is caused by fixed configuration and line broadening effects.

Propan-1-ol - Method A produced a poorly resolved quartet of basic pattern 1:3:3:1 ($a_{\text{H}} \sim 24$ Oe) with an additional central peak. Method C produced initially a spectrum identified as that of the ethyl radical ($a_{\text{CH}_2}^{\text{H}} = 19.8$, $a_{\text{CH}_3}^{\text{H}} = 26.4$ Oe) but an additional spectrum appeared on further photolysis. Method D yielded a mixture of three radicals as shown in figure 7 (e), consisting of $\text{NO}_2\cdot$ and $\text{C}_2\text{H}_5\cdot$ (identified from its two largest peaks separated by 26.4 Oe), and a basic five-line spectrum ($a_{\text{H}} = 22$ Oe) which is probably due to $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOH}$. The $\text{C}_2\text{H}_5\cdot$ signal decreased on standing in the dark at 77°K and upon warming the sample to ca. 175°K, only the five-line spectrum remained and is shown in figure 7 (f). The e.s.r. spectrum obtained on radiolysis of solid propan-1-ol exhibits five lines ($a_{\text{H}} = 21$ Oe)¹³² and is assigned to $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOH}$; similar results are obtained on photolysis of a propan-1-ol glass containing H_2O_2 .¹³⁴ The liquid phase spectrum produced in a similar manner to the ethanol radical shows six lines with $a_{\text{CH(OH)}}^{\text{H}} = 15.06$, $a_{\text{CH}_2}^{\text{H}} = 21.4$ Oe.¹²⁰

2-Methylpropan-1-ol - Method C produced a 1:2:1 triplet ($a_{\text{H}} = 20.2$ Oe) together with NO_2 and is shown in figure 7 (g). The radiolysis of solid isobutanol by Alger, Anderson and Webb¹³² produced an identical spectrum and experiments of a similar nature by Chacaty¹³³ also produced a basic triplet ($a_{\text{H}} = 21 \pm 1$ Oe) with some weak satellite lines. Accordingly, it appears that $(\text{CH}_3)_2\text{CH}\dot{\text{C}}\text{HOH}$ is formed, a radical characterised by both intense photolysis¹²⁰ and $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ oxidation flow techniques¹¹⁰ with $a_{\text{CH(OH)}}^{\text{H}} = 14.74$, $a_{\text{CH(Me)}_2}^{\text{H}} = 21.41$ Oe.

Butan-1-ol - Method C gave a five-line spectrum of approximate intensity distribution 1:2:2:2:1 ($a_{\text{H}} = 19$ Oe) together with an NO_2 spectrum (fig. 7 (h)). Radiolysis studies at 77°K of butan-1-ol¹³² produces a seven-line spectrum

with five central lines of comparable intensity and two weaker outermost lines but Chacaty¹³³ noted that on warming the sample to 120°K, the spectrum changed from a seven-line spectrum to a five-line spectrum. This change was attributed to a conversion from $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HOH}$. Low temperature H_2O_2 photo-oxidation experiments produced a poorly resolved spectrum¹³¹ consisting of six or seven lines with a_{H} ca. 20 Oe. It seems likely that the spectrum produced is, in fact, $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HOH}$. Solution studies for this radical report¹²⁰ $a_{\text{CH(OH)}}^{\text{H}} = 15.3$, $a_{\text{CH}_2}^{\text{H}} = 20.0$ Oe.

Pentan-1-ol - The spectrum obtained by method C is shown in figure 7 (b) and is almost identical with that found for butan-1-ol. Alger, Anderson and Webb¹³¹ found a strong similarity between e.s.r. spectra of butan-1-ol and pentan-1-ol following radiolysis, implying formation of structurally similar radicals $\text{RCH}_2\text{CH}_2\dot{\text{C}}\text{HOH}$ (R = Me or Et).

3.2.3. Secondary Aliphatic Alcohols

Propan-2-ol - Method A yielded initially the relatively narrow-lined quartet characteristic of $\text{CH}_3\dot{\text{C}}$ ($a_{\text{H}} = 23.0$ Oe) but a minor species was also present which increased in size relative to that of $\text{CH}_3\dot{\text{C}}$ on further photolysis, until both species were in comparable concentration.

The radical mixture illustrated in figure 8 (a) was analysed in terms of $\text{CH}_3\dot{\text{C}}$ ($a_{\text{H}} = 23.0 \pm 0.2$ Oe) and $\text{Me}_2\dot{\text{C}}\text{OH}$ ($a_{\text{CH}_3}^{\text{H}} = 20.0 \pm 0.5$ Oe) by means of a computer simulation (figure 8 (b)). Using method C, initial photolysis produced a radical mixture consisting of $\text{Me}_2\dot{\text{C}}\text{OH}$, $\text{CH}_3\dot{\text{C}}$ and $\text{NO}_2\dot{\text{C}}$. Method D yielded only $\text{CH}_3\dot{\text{C}}$ and $\text{NO}_2\dot{\text{C}}$. The averaged value of the coupling constant in $\text{Me}_2\dot{\text{C}}\text{OH}$ compares with values of 20 Oe obtained by other low temperature methods of generation.^{131, 132} The solution spectrum of $\text{Me}_2\dot{\text{C}}\text{OH}$ shows seven lines of binomial intensity with splitting constant $a_{\text{CH}_3}^{\text{H}} = 19.66$ Oe.¹²⁰

Butan-2-ol - Method A produced a broad and poorly resolved ethyl radical spectrum, whilst method C yielded a mixture of $\text{CH}_3\dot{\text{C}}$ ($a_{\text{H}} = 22.7 \pm 0.5$ Oe) and a 1:2:1 triplet ($a_{\text{H}} = 33.8$ Oe). Method D produced a poor $\text{CH}_3\dot{\text{C}}$ spectrum. Photolysis of butan-2-ol containing H_2O_2 ¹³¹ at 77°K gave a six-line spectrum and this radical is clearly not the one observed here.

3-Methylbutan-2-ol - Method C produced large $\text{CH}_3\dot{\text{C}}$ ($a_{\text{H}} = 22.8 \pm 0.3$ Oe) and very small $\text{NO}_2\dot{\text{C}}$ signals, the latter less than 5% of the total absorption.

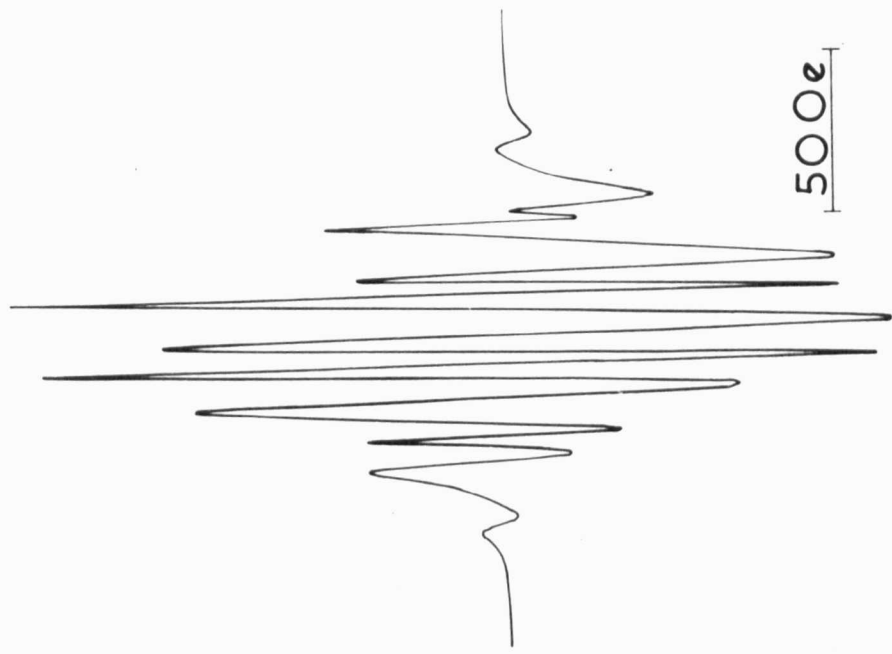
Pentan-3-ol - Method C yielded $\text{C}_2\text{H}_5\dot{\text{C}}$ with splittings $a_{\text{CH}_3}^{\text{H}} = 26.8 \pm 0.1$ Oe,

FIGURE 8

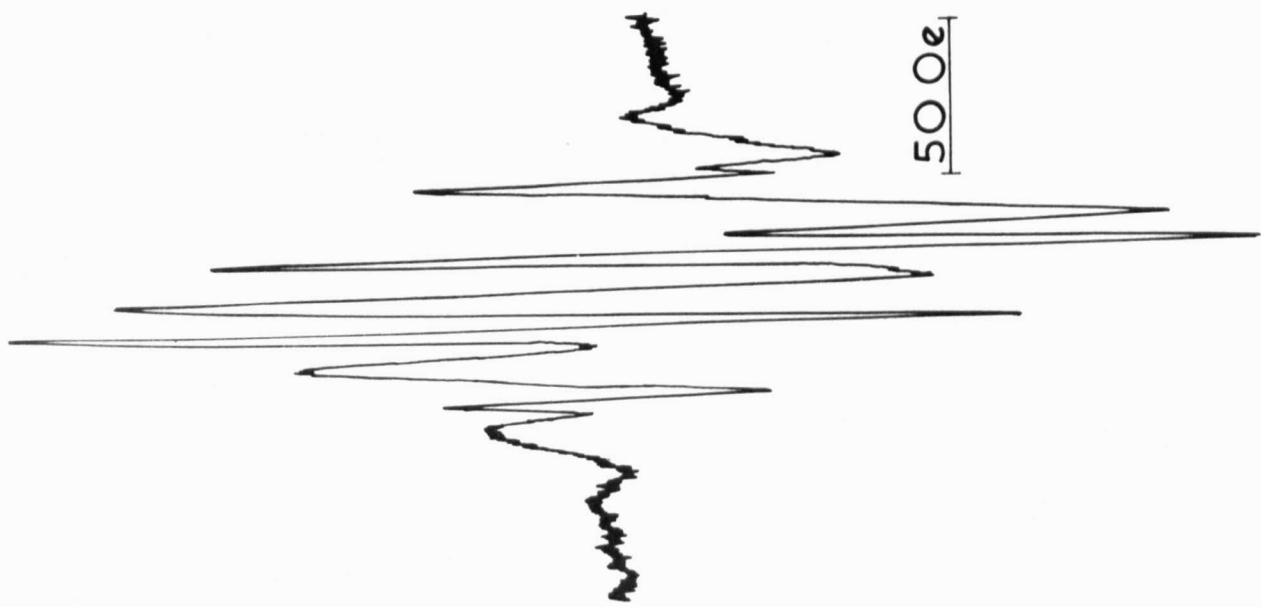
**E.S.R. Spectra Obtained During Photo-Oxidation of
Propan-2-ol by Ce^{IV}**

- (a) Experimental**
- (b) Computer Simulation**

(b)



(a)



$$a_{\text{CH}_2}^{\text{H}} = 20.5 \pm 0.2 \text{ Oe.}$$

Cyclohexanol - Method C produced a mixture of NO_2 and an eight-line spectrum. Gibson, Symons and Townsend¹³¹ obtained a six-line spectrum on low temperature photolysis of an H_2O_2 solution ($a^{\text{H}} = 20 \text{ Oe}$). This experiment was repeated and confirmed the observation of Symons et al.¹³¹ Our eight-line spectrum can be analysed in terms of $a_{\beta 1}^{\text{H}} = 35.6$, $a_{\beta 2}^{\text{H}} = 9.8 \text{ Oe}$ (2 protons each) producing nine lines, the first line of the spectrum being under the low field NO_2 peak. γ -irradiation of cyclohexanol¹³⁴ at 77°K produced a similar spectrum with $a_{\beta 1}^{\text{H}} = 36.1 \text{ Oe}$, $a_{\beta 2}^{\text{H}} = 10.0 \text{ Oe}$, which changed slowly upon u.v. irradiation to a six-line spectrum attributed to the 2-cyclohexanol radical, and it seems likely that the six-line spectrum observed on photolysis of cyclohexanol and H_2O_2 is also due to the 2-cyclohexanol radical. Accordingly, the spectrum produced from photo-oxidation by Ce^{IV} is ascribed to the 1-cyclohexanol radical.

3.2.4. Tertiary Aliphatic Alcohols

Tert-butanol - Photolysis at 77°K under all experimental conditions led to the immediate production of a 1:3:3:1 quartet with $a_{\text{H}} = 22.7 \pm 0.3 \text{ Oe}$ identified as the CH_3^\cdot radical. Method C produced, in addition, a minor spectrum which intensified on continued photolysis, e.g. for 15 minutes, to yield a 1:2:1 triplet of overall width 42 Oe. Warming a photolysed aqueous ceric ammonium nitrate sample to 180°K resulted in the disappearance of CH_3^\cdot and production of a similar 1:2:1 triplet. Standing a sample prepared by method C and irradiated for only four seconds (to produce a "pure" CH_3^\cdot spectrum) for a period of twenty-seven hours at 77°K also led to the same triplet at the expense of CH_3^\cdot (figure 9), which was further produced by photolysis of ceric ammonium nitrate in neat tert-butanol at 245°K . The triplet originates from a $\text{CH}_2\text{X}^\cdot$ species, the most likely candidate being $\text{CH}_2\text{CMe}_2\text{OH}^\cdot$ for which a coupling constant of $a_{\text{CH}_2}^{\text{H}} = 21.3 \text{ Oe}$ has been reported in water at 293°K .¹¹⁰

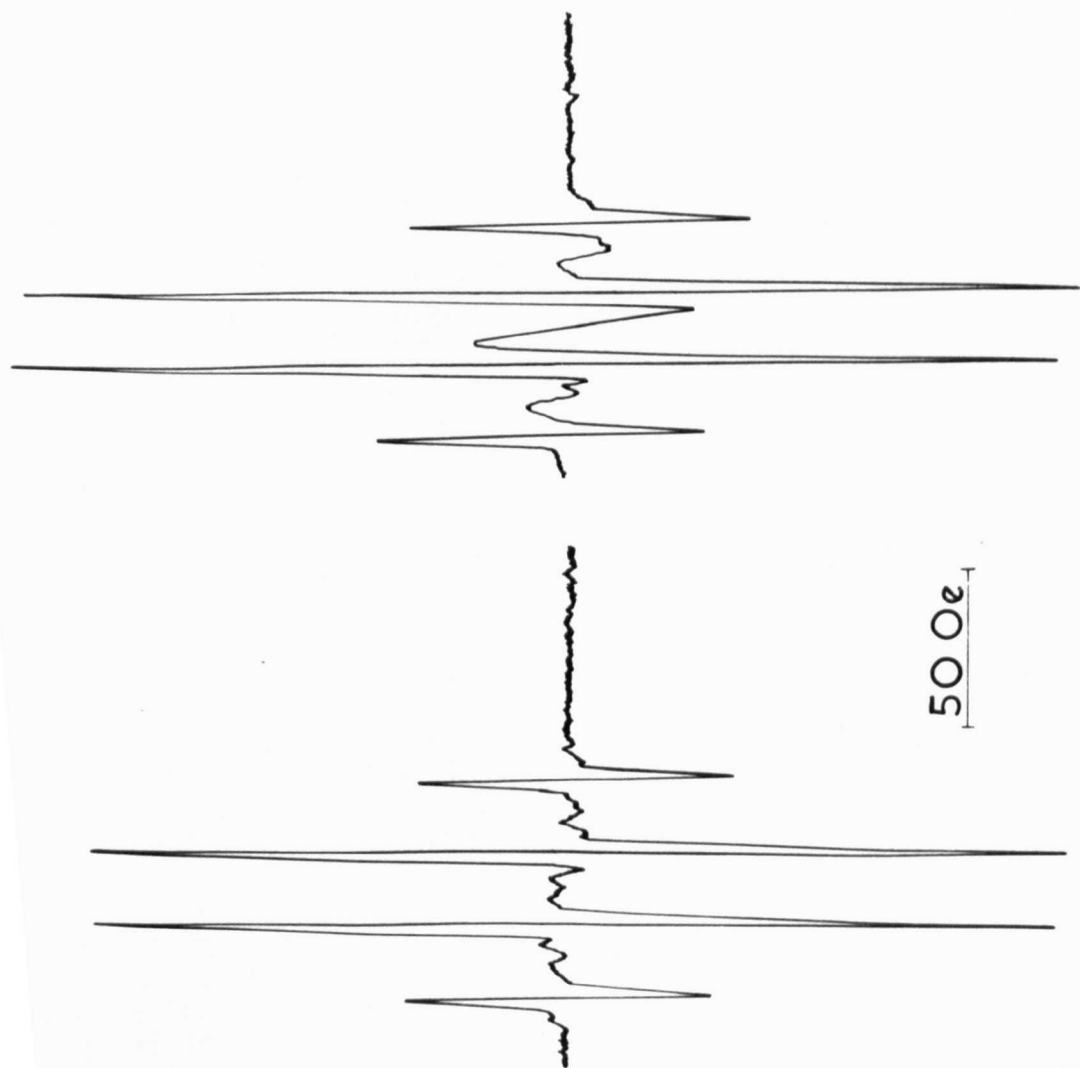
3-Ethylpentan-3-ol - Study by methods A, B and C produced the spectrum of $\text{C}_2\text{H}_5^\cdot$ with $a_{\text{CH}_3}^{\text{H}} = 26.5 \pm 0.3$, $a_{\text{CH}_2}^{\text{H}} = 21.0 \pm 0.3 \text{ Oe}$.

1,1-Dimethylpropan-1-ol - Method C gave an ethyl radical shown in figure 10 (a) with $a_{\text{CH}_3}^{\text{H}} = 26.3 \pm 0.3$, $a_{\text{CH}_2}^{\text{H}} = 20.8 \pm 0.3 \text{ Oe}$. Method A, however, produced a 1:3:3:1 quartet with $a_{\text{H}} = 23.3 \text{ Oe}$; this suggests CH_3^\cdot is formed,

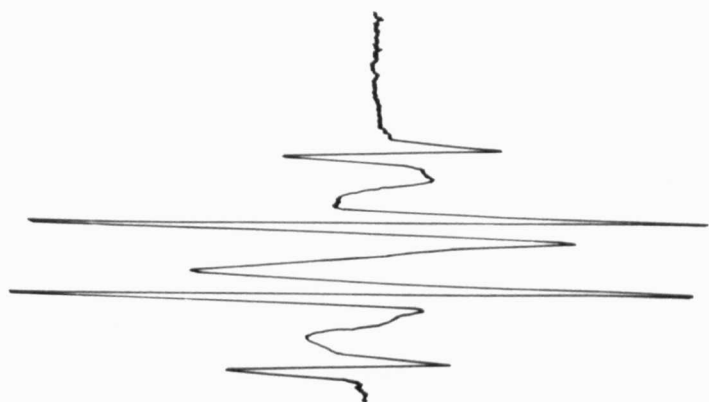
FIGURE 9

**Decay in the Dark of E.S.R. Spectrum of Methyl Radical
in *t*-Butanol Following Photo-Oxidation by Ce^{IV}**

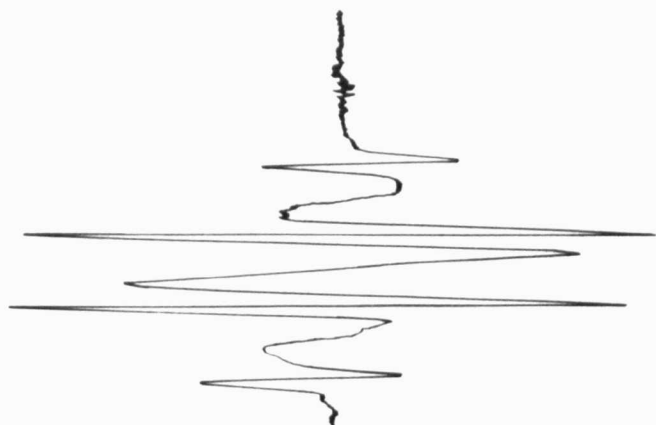
- (a) Immediately after 4s of photolysis**
- (b) 3 hours later**
- (c) 19 hours later**
- (d) 27 hours later**



(a)



(c)



(d)

but the peaks were unusually broad and the outermost peaks were partially split into doublets.

3-Methylhexan-3-ol - Method C gave a spectrum (shown in figure 10(b)) consisting of a mixture of $C_2H_5\cdot$ identified by the coupling constant of the two most intense peaks ($a_{CH_3}^H = 27.0 \pm 0.3$ Oe) and a 1:2:1 triplet with $a_H \sim 24$ Oe.

2,3-Dimethylbutan-2-ol - Whilst method A gave only a poorly resolved spectrum, method C gave a nine-line spectrum shown in figure 10(c) of overall width 120 Oe. This is due to a mixture of radicals, one of which displays a basic seven-line spectrum of binomial character ($a^H \sim 20$ Oe) and which cannot therefore be $Me_2\dot{C}H$ known to exhibit an eight-line spectrum with $a_H = 26.4$ Oe.¹⁰⁷

1-Ethynylcyclohexanol - Method E produced a spectrum of NO_2 and $\dot{C}H_2CN$. Photolysis of a "blank" solution of ceric ammonium nitrate in CH_3CN for a comparable period of time gave no signal. The $\dot{C}H_2CN$ radical presumably comes from attack by the ethynyl radical, which has only been obtained by trapping in an argon matrix at $12^\circ K$ ¹³⁵ and it seems likely that it is sufficiently mobile and reactive at $77^\circ K$ to abstract from CH_3CN to produce, as the only observable species, $\dot{C}H_2CN$.

3.2.5. Allylic and Acetylenic Alcohols

Allyl Alcohol - Methods A, C and D all resulted in production of a four-line spectrum of total width 44.3 Oe (figure 11(a)) and identical in appearance and width with that reported by Maas and Volman using H_2O_2 photo-oxidation at $125^\circ K$,¹³⁶ and by other groups using similar techniques.^{137,138} It is assigned to the allyl-type radical $\dot{C}H_2=CH-CHOH$.

But-2-en-1-ol - Method A produced a broad spectrum at $77^\circ K$ showing only slight structure, but subsequent warming to $193^\circ K$ yielded a six-line spectrum shown in figure 11(b) of total width 77 ± 1 Oe, ($a_H = 15.4$ Oe). This is identical with the spectrum obtained by photo-oxidation of crotyl alcohol by H_2O_2 and observed at $122^\circ K$ ¹³⁶ (total width 75 Oe) and is assigned to $\dot{C}H_3-CH=CH-CHOH$ with five protons being approximately equivalent.

But-3-en-2-ol - Method C gave a partly resolved six-line spectrum at $77^\circ K$, but subsequent warming to $130^\circ K$ resulted in improved resolution illustrated in figure (c), and an overall width of 71 Oe was obtained with $a_H = 14.3$ Oe. A similar spectrum of 70 Oe width was obtained on low-temperature oxidation by OH .¹³⁶ The spectrum is attributed to

FIGURE 10

**E.S.R. Spectra Obtained During Photo-Oxidation of
Tertiary Alcohols by Ce^{IV}**

- (a) 1,1-Dimethylpropan-1-ol**
- (b) 3-Methylhexan-3-ol**
- (c) 2,3-Dimethylbutan-2-ol**

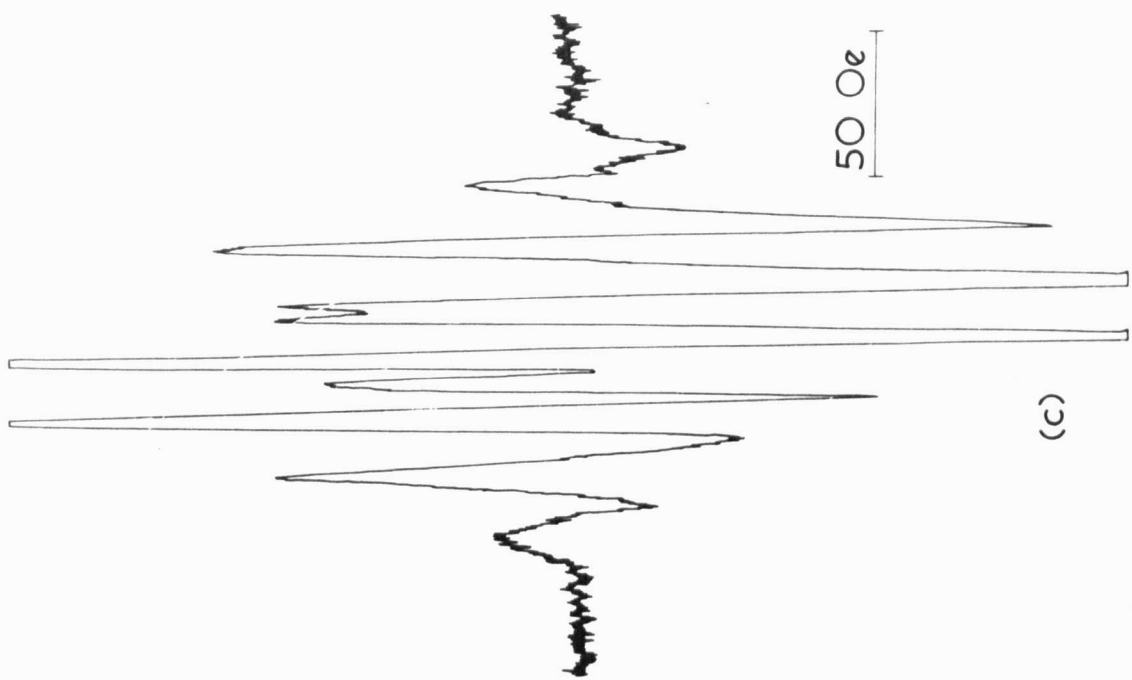
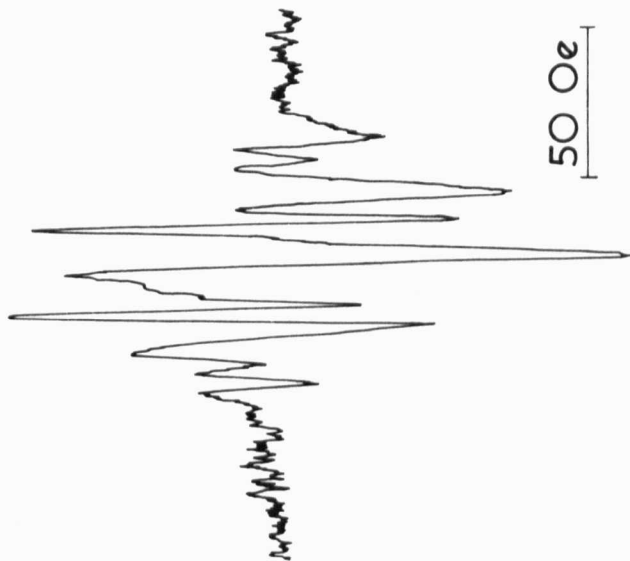
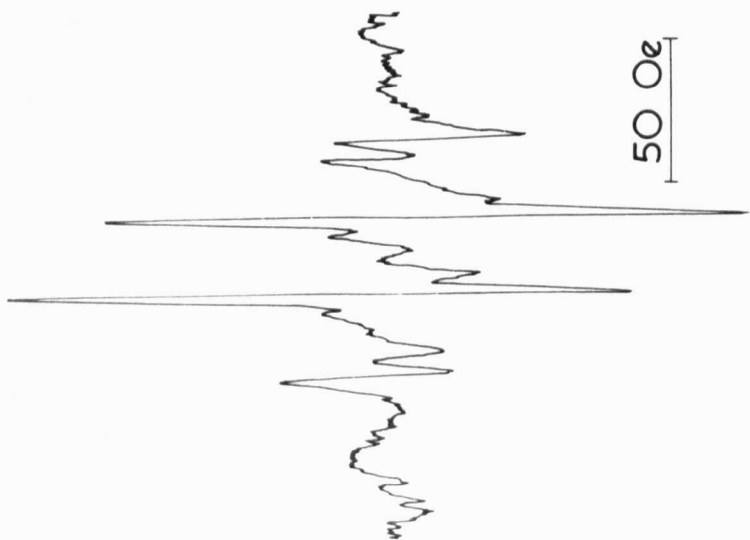


FIGURE 11

**E.S.R. Spectra Obtained During Photo-Oxidation of
Allylic Alcohols by Ce^{IV}**

- (a) Allyl Alcohol**
- (b) But-2-en-1-ol (193°K)**
- (c) But-3-en-2-ol (130°K)**

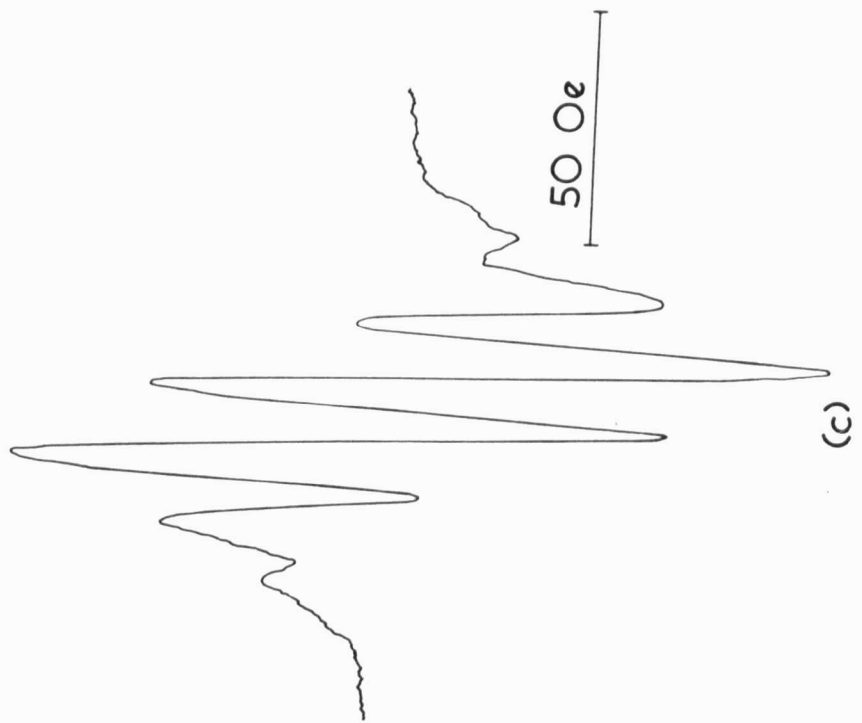
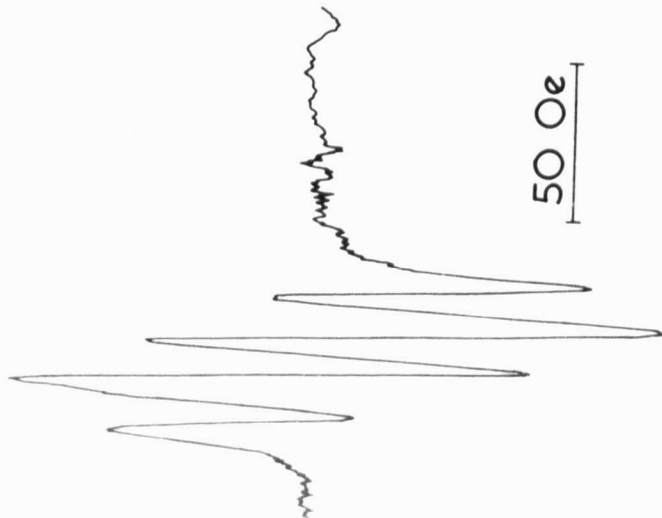
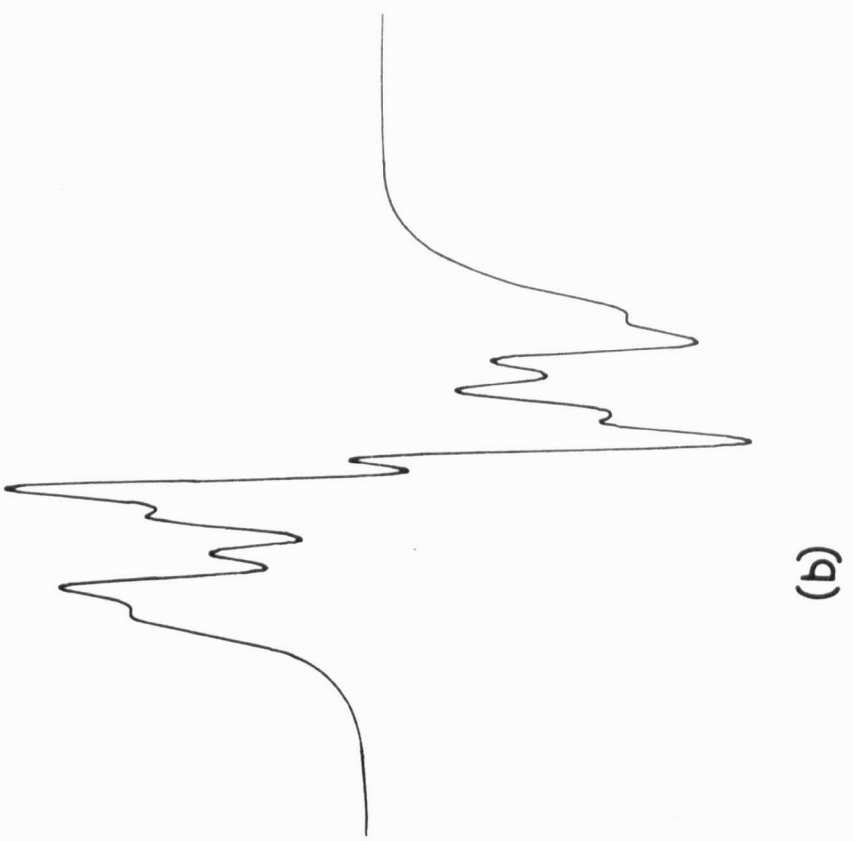
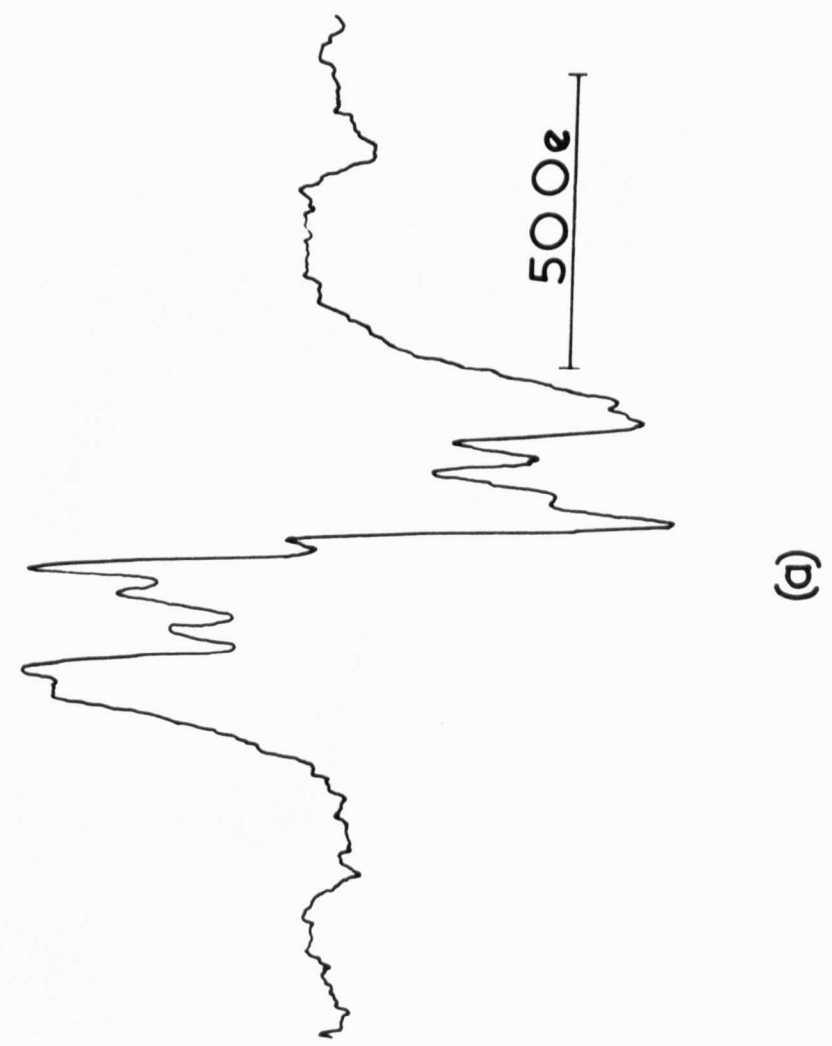


FIGURE 12

**E.S.R. Spectrum of Benzyl Radical Obtained During
Photo-Oxidation of 1,2-Diphenylethanol by Ce^{IV}**

(a) Experimental

(b) Computer Simulation

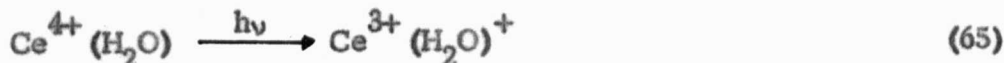


DISCUSSION

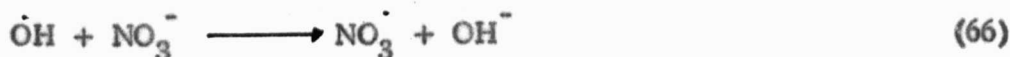
The photochemistry of one-equivalent oxidising metal ions is dominated by electron transfer to metal-ion processes, particularly for d^{10} systems, where there can be no complicating photosubstitution processes and also with wavelengths $\lambda < 400$ nm where C-T bands tend to absorb strongly. Ce^{IV} is a singularly good example of such an ion and photolysis in the presence of simple ligands such as NO_3^- results in net transfer of an electron and production of a small inorganic radical like NO_3^\cdot , identified by optical and e.s.r. spectroscopy in liquid⁶⁷ and frozen solutions.⁶⁸ The production of NO_3^\cdot has been suggested to occur via attack on the nitrate ion by \dot{OH} , produced from oxidation of ligand water,⁶⁵ viz.



or in frozen solutions at 77°K,



followed by,



The detection of H_2O^+ by e.s.r.⁶⁶ has given credence to the production of \dot{OH} as the primary process. However, this remains controversial⁶⁸ and the reactions observed with ceric ammonium nitrate dissolved in neat organic solvent rule out the production of \dot{OH} .

Recently the hydronium radical, H_3O^\cdot , ($a_H = 22.84$, $g = 2.0034$) has been observed after annealing photolysed ceric perchlorate glasses;¹⁴³ however, photolysis of Ce^{IV} in a 99.8% deuterated medium produced not D_3O^\cdot and D_2HO^\cdot as the main radical species but H_3O^\cdot and H_2DO^\cdot . This most unexpected result has not yet been explained. However, the production of H observed in the "blank" experiments (page 29), could come from dissociation of H_3O^\cdot ,



Solutions of Ce^{IV} perchlorate and nitrate form C-T complexes with

alcohols (page 7), shifting the absorption to the visible (λ_{\max} ca. 320 nm) and increasing the extinction respectively, to impart an orange-red colour. Irradiation with light of $\lambda > 300$ nm eliminates any tendency to photolyse the organic substrate directly and use of 4 M HClO_4 reduces the contribution from species such as $\text{Ce}(\text{OH})^{3+}$ and it is reasonably certain that the radicals observed are those produced by a genuine CTM process. Ceric ammonium nitrate shows C - T bands with the nitrate ligand ($\epsilon_{\max} = 3580 \pm 50$, $\lambda_{\max} = 285$ nm) and the production of nitrogen-containing radicals upon irradiation of "blank" solutions shows some degree of photo-oxidation. However, the increased extinction ($\epsilon_{\max} = 4130 \pm 50$, 4650 ± 50 for ethanol and propanol respectively) of the alcohol-containing solutions, and the production of organic radicals in concentrations very much greater than NO_2 , implies a preferential absorption of light by the alcohol complexes. The similarity of the behaviour of both Ce^{IV} perchlorate and nitrate solutions containing alcohols is a reasonable indication that the nitrate ligands do not greatly affect the photochemistry, although the presence of wing peaks of ca. 120 Oe separation, in varying concentrations, in experiments involving the nitrate ion, could be adduced as evidence for electron transfer from NO_3^- to Ce^{IV} operating in parallel with that from the organic ligand.

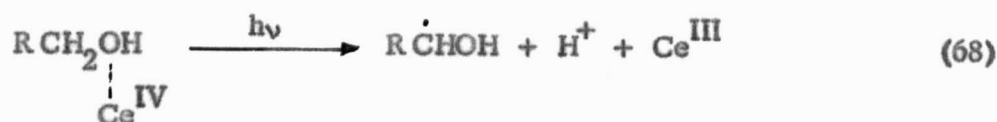
The assignment of these peaks to NO_2^\cdot rests on the following evidence :

- (i) The particularly intense spectrum obtained from benzyl alcohol by method C could be analysed by the method of Kneubühl¹⁰² as follows : $g_1 = 2.006$, $g_2 = 2.002$, $g_3 = 1.995$ (all ± 0.001), $a_1^{\text{N}} = 48.9$, $a_2^{\text{N}} = 64.5$, $a_3^{\text{N}} = 43.2$ Oe (all ± 0.5 Oe). These values are similar to those reported by Ayscough and Collins¹⁴⁴ for NO_2^\cdot in an alkaline glass at 77°K following photolysis of $\text{Fe}(\text{CN})_6^{4-}$ ions in the presence of NO_3^- ions, and also those of many other authors.
- (ii) The spectrum of NO_3^\cdot , the principal nitrogen radical expected, is much narrower, having $g = 2.002$, $g = 1.995$ (all ± 0.001) and exhibiting small hyperfine splitting ($a_{\text{iso}} = 3.74$ Oe). This species was produced by photolysis in a "soft" lattice of HNO_3 and HClO_4 with irradiation of 320 - 420 nm, of 10^{-2} M ceric ammonium nitrate.⁶⁸ Continued photolysis in this region did not result in any transformation of NO_3^\cdot into NO_2^\cdot which implies

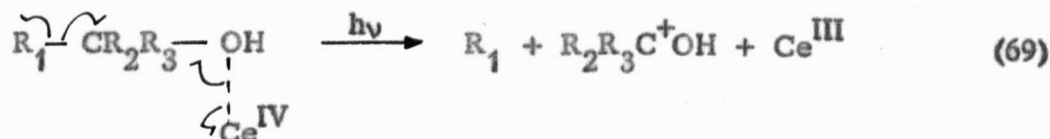
that NO_2 produced in this work is not a product of secondary photolysis of NO_3 (which is photolysed with $\lambda > 490 \text{ nm}$ to give diamagnetic products.)

The origin of the NO_2 signal is problematic ; a strong signal was obtained from a solution of ceric ammonium nitrate in benzyl alcohol even when a filter transmitting only light beyond 360 nm was used, conditions normally giving rise only to NO_3 in acid glasses.⁷ It seems possible that a small fraction of the organic radicals produced are able to reduce neighbouring NO_3^- ions to NO_2 and OH^- , and being oxidised themselves to diamagnetic carbonium ions.

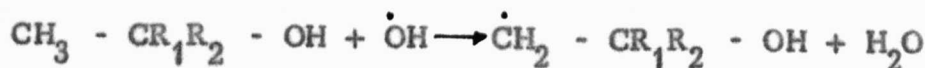
The photo-oxidation of simple aliphatic primary alcohols can be written :



and the observation of the corresponding hydroxy-alkyl radical with all the primary alcohols used shows that this is, in fact, the main mechanism operating at 77°K . However, production of CH_3 (from ethanol) and C_2H_5 (from propanol) indicates a second pathway more akin to the photo-oxidation of secondary and tertiary alcohols which may be expressed as :



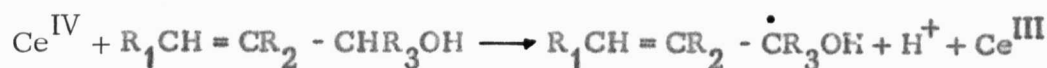
and the extremely prompt appearance of CH_3 from tertiary butanol suggests a concerted mechanism (equation (69)). The intermediate $\text{R}_1\text{R}_2\text{R}_3\text{CO}^\bullet$ has been postulated during anodic oxidation of tertiary alcohols,¹⁴⁵ but no e.s.r. signal due to the alkoxy radical was observed in this work. The primary production of alkyl radicals during oxidations of secondary and tertiary alcohols by Ce^{IV} contrasts with the behaviour of OH which oxidises alcohols exclusively by hydrogen abstraction, both in solid matrices¹³¹ and in solution,^{110, 120} viz.



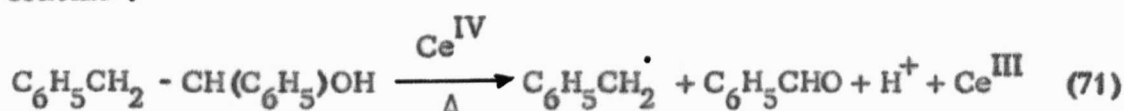
and this behaviour rules out the intermediacy of OH in photo-oxidations by ceric perchlorate.

A close similarity does exist between Ce^{IV} and $\dot{\text{O}}\text{H}$ in the oxidation of

allylic alcohols to their corresponding hydroxyallyl radicals by a process analogous to equation (68).



The photo-oxidation of alcohols by Ce^{IV} bears a close resemblance to the thermal oxidations by one-electron oxidants such as Co^{III} , V^{V} , Mn^{III} and Ce^{IV} itself.¹⁴⁶ Both reactions proceed through a 1:1 complex and both involve C-H and C-C bond cleavage reactions, C-C bond cleavage occurring to a greater extent with the more highly substituted alcohols and being the only mode of reaction with tertiary alcohols. From kinetic rate data the rate-determining step in the oxidation of, for example, tertiary butanol and 2-methylbutan-2-ol,¹⁴⁷ by Co^{III} , was shown to be the production of CH_3 and C_2H_5 respectively and this is borne out in the photo-oxidation of these by Ce^{IV} . C-C bond cleavage has also been noted in the Co^{III} oxidation of propan-2-ol and butan-2-ol.¹⁴⁷ The corresponding thermal reactions with Ce^{IV} ^{148,149} have produced no evidence of C-C bond cleavage, though this is due to the inability of the analytical method employed¹⁵⁰ to distinguish between any aldehydes and ketones produced. A further analogy between thermal and photochemical oxidation is instanced by 1,2-diphenylethanol which undergoes thermal oxidation with Ce^{IV} ⁵¹ according to the scheme :



and the benzyl radical produced on photo-oxidation is shown in figure 12.

Similar behaviour is observed during photo-oxidation of 2-phenylethanol which is oxidised thermally by V^{V} ⁵⁵ to the benzyl radical and ~~benzaldehyde~~^{+formaldehyde}. Of the other benzylic alcohols, 1,1-diphenylethanol might be expected to break down on photo-oxidation to phenyl or methyl radical; however, the observation of only CH_2CN implies production of phenyl radical which, even at 77°K, is sufficiently reactive to attack hydrogen-containing molecules of the matrix.¹⁵¹ This type of reaction is also noted with 1-ethynyl-1-cyclohexanol when the ethynyl radical abstracts from the solvent to form $\dot{\text{C}}\text{H}_2\text{CN}$ in a similar manner.

Secondary reactions are also noted with CH_3 , produced from tert-butanol, which slowly attacks the alcohol matrix to produce $\text{CH}_2\text{CMe}_2\text{OH}$ as shown in figure 9.

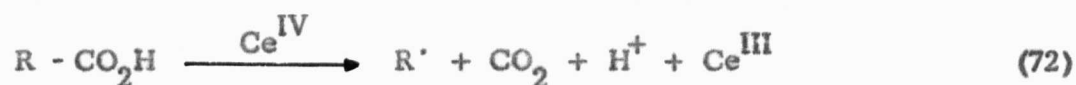
CHAPTER 4

Ce^{IV} PHOTO-OXIDATION OF CARBOXYLIC ACIDS

4. Ce^{IV} PHOTO-OXIDATION OF CARBOXYLIC ACIDS

4.1 Introduction

The thermal oxidation of carboxylic acids by Ce^{IV} is slow, and simple aliphatic acids are stable to refluxing ceric sulphate. The photosensitivity of ceric carboxylates is unusually high, for example, $\phi_{\text{CO}_2} = 1.11 \pm 0.07$ for pivalic acid, and the photodecomposition is believed to lead to the production of CO_2 and an alkyl radical on the basis of the distribution of products (page 8) viz.



An analogous process has already been shown to occur during photolysis of frozen solutions of lead tetraacetate in carboxylic acids,¹⁵² the radicals produced being stabilised in the matrix and observed by e.s.r. spectroscopy, and it is the purpose of this chapter to illustrate the primary processes during Ce^{IV} photo-oxidation of carboxylic acids.

The methods of sample preparation have been described in chapter 3; for convenience, most acids were examined in aqueous solution using ceric perchlorate to eliminate confusion of the spectra with NO_2 absorptions produced by ceric ammonium nitrate. Unless otherwise stated, all reactions were carried out by method A (page 29). These particular samples rarely formed good glasses and the high signal-to-noise ratio obtained with some samples is a measure of the photosensitivity of these systems.

4.2 Results

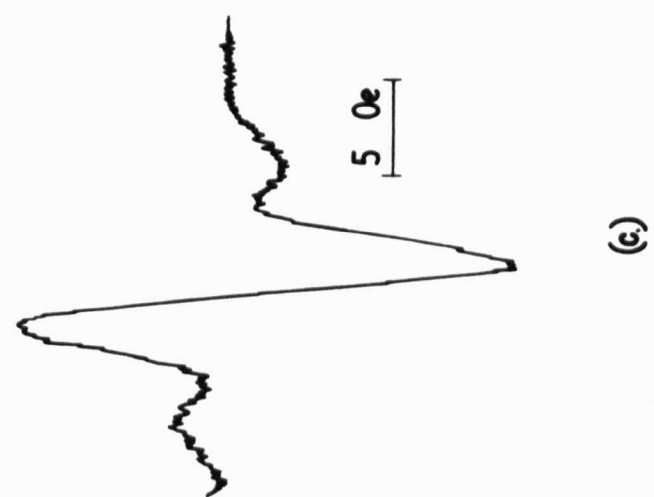
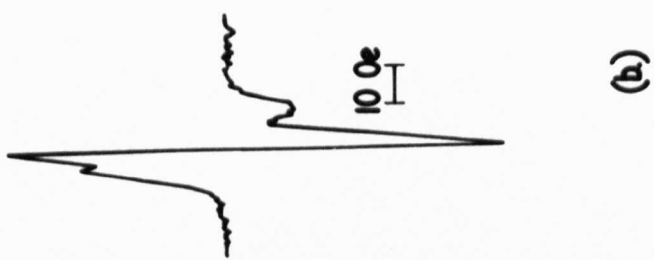
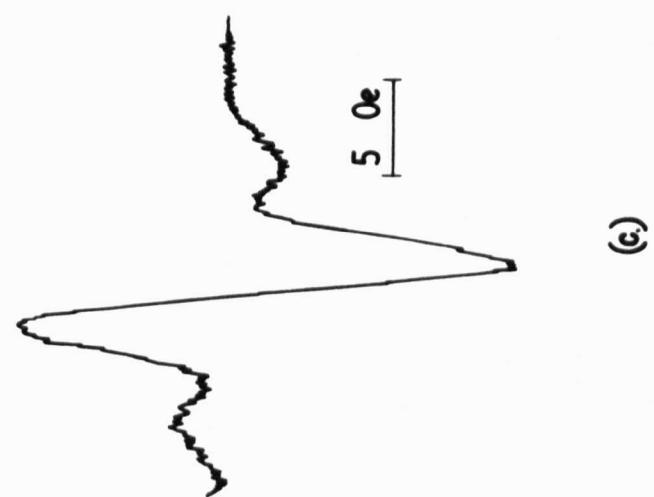
4.2.1. Saturated Aliphatic Acids

Formic Acid - (a) Experiments with $\lambda > 360$ nm and with short irradiation times. Photolysis of HCO_2H in aqueous $(\text{H}_2\text{O})\text{HClO}_4$ at 77°K produced broad H-atom signals (line width 3.0 ± 0.2 Oe) with $a_{\text{H}} = 504 \pm 2$ Oe, each exhibiting two satellite peaks (figure 13(a)) not quite symmetrically placed about the central line with $a_{\text{H}} = 6.2 \pm 0.1$ Oe (high-field component of each group) and 5.5 ± 0.1 Oe (low-field component of each group). In a medium consisting of 95% D_2O and DClO_4 , the H-atoms showed no satellite lines and a reduced width of 1.2 ± 0.2 Oe. In a 50% isotopically substituted medium, the line width was 2.4 ± 0.2 Oe and the satellites, while still present and exhibiting

FIGURE 13

**E.S.R. Spectra Obtained During Photo-Oxidation of
Formic Acid by Ce^{IV}**

- (a) Formic Acid ($\lambda > 360 \text{ nm}$)**
- (b) Formic Acid ($\lambda > 300 \text{ nm}$)**
- (c) Formic Acid-d ($\lambda > 300 \text{ nm}$, high
field peak of triplet of D^\bullet)**



the same coupling, were much weaker in intensity relative to the central peak of each group of lines. On warming to 115°K , the H-atoms disappeared but a new spectrum appeared to high field of $g = 2$, denoted spectrum C.

(b) Experiments with $\lambda > 300\text{ nm}$. In addition to H-atom signals, additional absorptions due both to formyl radical and a narrow central spectrum displaying some structure were observed (fig. 13 (b)). The narrow spectrum is identical to spectrum C described above. On warming to 115°K , both H \cdot and HCO disappeared to leave spectrum C, now enhanced in intensity, which itself disappeared when the temperature was raised to 175°K .

Deuteroformic Acid - Irradiation with light of $\lambda > 360\text{ nm}$ of a solution of DCO_2H in H_2O and HClO_4 containing Ce^{IV} yielded the characteristic three-line spectrum of D \cdot ($a_{\text{D}} = 76.6\text{ Oe}$) showing weak hyperfine splitting of each line. Experiments with light of $\lambda > 300\text{ nm}$ yielded only D-atoms but in greater yield. Each of the lines displayed satellite peaks with $a_{\text{H}} = 6.1 \pm 0.1\text{ Oe}$ (high-field satellite) and $a_{\text{H}} = 5.5\text{ Oe}$ (low-field satellite). The line width of the high field peak is 2.9 Oe (figure 13 (c)). On warming the sample to 115°K , the D-atoms decayed and a new spectrum emerged identical to that shown in figure 13 (b), for spectrum C.

Spectrum C is due to a species found in photo-oxidised HCO_2H and DCO_2H systems either with short wavelength light (for HCO_2H) or on allowing H \cdot or D \cdot to decay at 115°K . Analysis of spectrum C yields $g_1 = 2.0052$, $g_2 = 2.0016$ and $g_3 = 1.9951$ (all ± 0.0005).

Acetic Acid - While method A yielded only a strong quartet of intensity distribution 1:3:3:1 with $a_{\text{H}} = 22.8 \pm 0.2\text{ Oe}$ which can be unambiguously attributed to the methyl radical, method C produced, in addition to $\text{CH}_3\cdot$, three smaller peaks positioned midway between those of the quartet of $\text{CH}_3\cdot$ with $a_{\text{H}} = 22.0\text{ Oe}$. Method D resulted in the two radicals found by method C but with the $\text{CH}_3\cdot$ and triplet signals in comparable intensity; the triplet could now be seen to be of an approximate 1:2:1 character consistent with an assignment to $\cdot\text{CH}_2\text{CO}_2\text{H}$ for which a_{H} in solution is 21.8 Oe .¹¹¹

Propionic Acid - Photolysis at 77°K produced only $\text{C}_2\text{H}_5\cdot$ with $a_{\text{CH}_3}^{\text{H}} = 26.5$, $a_{\text{CH}_2}^{\text{H}} = 20.9\text{ Oe}$. Photolysis of a methanolic solution of propionic acid and ceric perchlorate at 175°K yielded a spectrum of $\text{C}_2\text{H}_5\cdot$ consisting of

much narrower lines.

Butyric Acid - A six-line spectrum was obtained of $a_{\text{average}}^{\text{H}} = 23.0$ Oe which is similar in appearance to that obtained by Ayscough and Thomson¹⁰⁴ on γ -radiolysis of n-propyl bromide at 77°K with $a_{\text{average}}^{\text{H}} = 24$ Oe and assigned to n-propyl radical. Computer simulation of our six-line spectrum gave $a_{\alpha\text{H}} = 20.0$, $a_{\beta_1\text{H}} = 24.9$, $a_{\beta_2\text{H}} = 45.0$ Oe showing that at 77°K the two β -protons are inequivalent. The solution spectrum of n-propyl radical¹⁰⁵ produced by continuous irradiation of propane with 2.8 Mev electrons gives $a_{\alpha\text{H}} = 22.08$, $a_{\beta\text{H}} = 33.2$ Oe.

Isobutyric Acid - An eight-line spectrum of $a_{\text{average}}^{\text{H}} = 24.3$ Oe was obtained, similar to that published by Ayscough and Thomson¹⁰⁴ from γ -irradiated isopropyl bromide ($a_{\text{average}}^{\text{H}} = 26.4$ Oe), which is assigned to the isopropyl radical.

Pivalic Acid - A ten-line spectrum of binomial intensity was obtained ($a_{\text{H}} = 21.7$ Oe) which is due to t-butyl radical.

4.2.2. Alicyclic Acids

Cyclopropanecarboxylic Acid - The resulting spectrum given in fig. 14 (a) is readily analysed in terms of coupling from a single proton ($a_{\text{H}} = 5.4$ Oe) and from four equivalent protons ($a_{\text{H}} = 22.1$ Oe). Assignment of the trapped species to cyclopropyl radical is supported by comparison with the coupling constant, published by Fessenden and Schuler¹⁰⁵ for this species, which was obtained as a component of a complex radical mixture on electron irradiation of cyclopropane at 153°K ($a_{\text{H}} = 6.5$, $a_{\text{H}} = 23.4$ Oe). Cyclopropane is unusually inert to attack by photo-generated t-butoxyl radical and this "pure" spectrum may be unique.

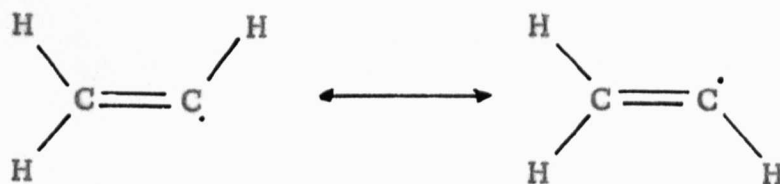
Cyclobutanecarboxylic Acid - The experimental spectrum and a computer simulation of it are shown in figures 14 (b) and (c) respectively. The measured coupling constants are 36.5 Oe (four protons) and 21.0 Oe (one proton). Coupling from the two other protons is estimated to be < 1.0 Oe. The liquid phase spectrum of electron-irradiated cyclobutane¹⁰⁵ at 193°K is due to several radicals but the contribution of the cyclobutyl radical, with coupling constants of 21.2, 36.66, and 1.12 Oe for one, four, and two protons respectively, makes it clear that our spectrum at 77°K is also that of cyclobutyl radical.

Cyclopentanecarboxylic Acid . - The eight-line spectrum $a_{\text{average}}^{\text{H}} = 23.1 \text{ Oe}$ shown in figure 14 (d) is identical with that obtained by Ayscough and Thomson on γ -radiolysis of cyclopentyl bromide at 77°K ($a_{\text{average}}^{\text{H}} = 22.9 \text{ Oe}$). Computer simulation of the spectrum was achieved with $a_{\alpha\text{H}} = 29.9$, $a_{\beta_1\text{H}} = 46.0$, $a_{\beta_2\text{H}} = 23.0 \text{ Oe}$ and the spectrum is assigned to the cyclopentyl radical.

Cyclohexanecarboxylic Acid - The six-line spectrum with $a_{\text{average}}^{\text{H}} = 21.0 \pm 0.8 \text{ Oe}$ shown in figure 14 (e) compares well with the Ayscough and Thomson¹⁰⁴ spectrum of the cyclohexyl radical ($a_{\text{average}}^{\text{H}} = 25.0 \text{ Oe}$). A computer simulation of the radical obtained from cyclohexanecarboxylic acid ($a_{\text{H}\alpha} = 21.0$, $a_{\text{H}\beta_1} = 38.7$, $a_{\text{H}\beta_2} = < 1 \text{ Oe}$) is depicted in figure 14 (f).

4.2.3. Unsaturated Acids

Acrylic Acid - The spectrum obtained at 77°K is depicted in figure 15 (a) and is analysed in terms of three nonequivalent protons with couplings of 15.6, 38.0 and 66.5 Oe. These coupling constants compare with those of 16, 34 and 68 obtained by Cochran, Bowers and Adrian¹⁵³ for vinyl radical on photolysis of NI in the presence of acetylene in an argon matrix at 4°K . Fessenden and Schuler¹⁰⁵ obtained a four-line liquid phase spectrum at 93°K as a minor species in the electron irradiation of a mixture of ethylene and ethane with coupling constants of 13.4 and 102.4 Oe; the latter is regarded as the sum of two proton splittings which are broadened by rapid inversion of the methine proton in the liquid,



Warming to 153°K effected a broadening in the central lines, leaving only the four outmost lines ($a_{\beta}^{\text{H}} = 101.0$ and $a_{\alpha}^{\text{H}} = 14.3 \text{ Oe}$) indicating that the situation found by Fessenden and Schuler had just begun to emerge. In contrast, Bennett and Mile¹⁵⁴ find that vinyl radicals prepared by the rotating cryostat technique exhibit the four-line spectrum at 77°K . Continued warming to 175°K in the dark led to the production of another radical characterised by five lines ($a_{\text{H}} = 21.4 \text{ Oe}$) with approximate line intensities 1 : 2 : 2 : 2 : 1. Warming to 220°K effected complete decay of this radical.

FIGURE 14

**E.S.R. Spectra Obtained During Photo-Oxidation of
Alicyclic Acids by Ce^{IV}**

- (a) Cyclopropanecarboxylic Acid**
- (b) Cyclobutanecarboxylic Acid (experimental)**
- (c) Computer Simulation of (b)**
- (d) Cyclopentanecarboxylic Acid**
- (e) Cyclohexanecarboxylic Acid (experimental)**
- (f) Computer Simulation of (e)**

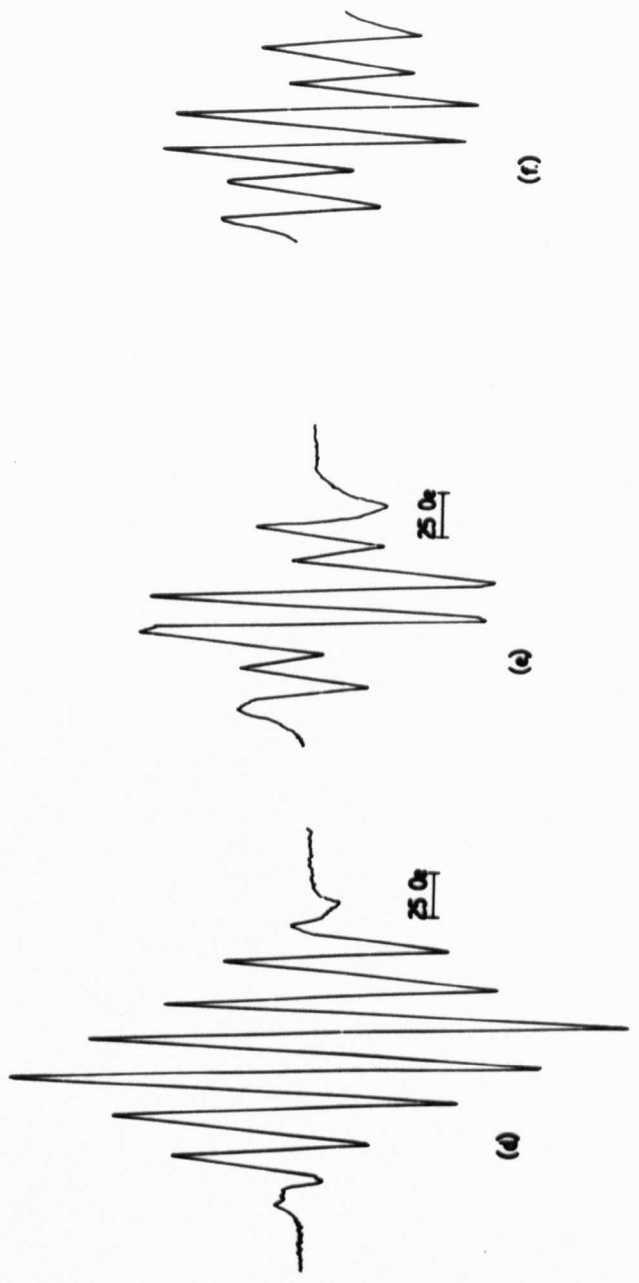
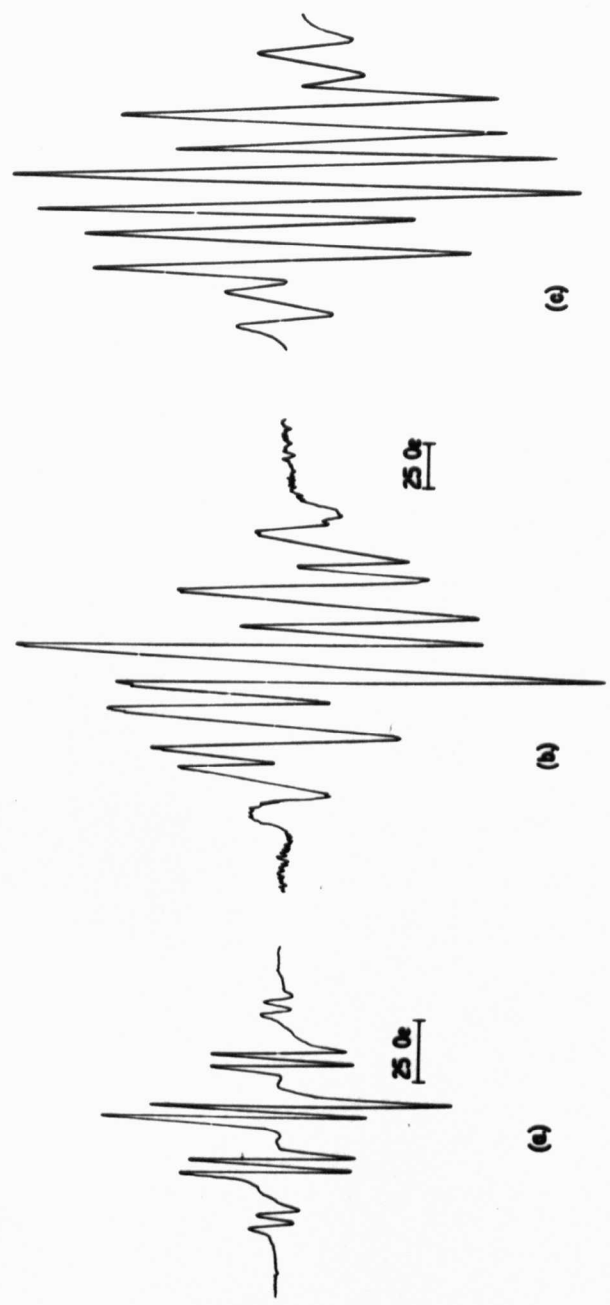
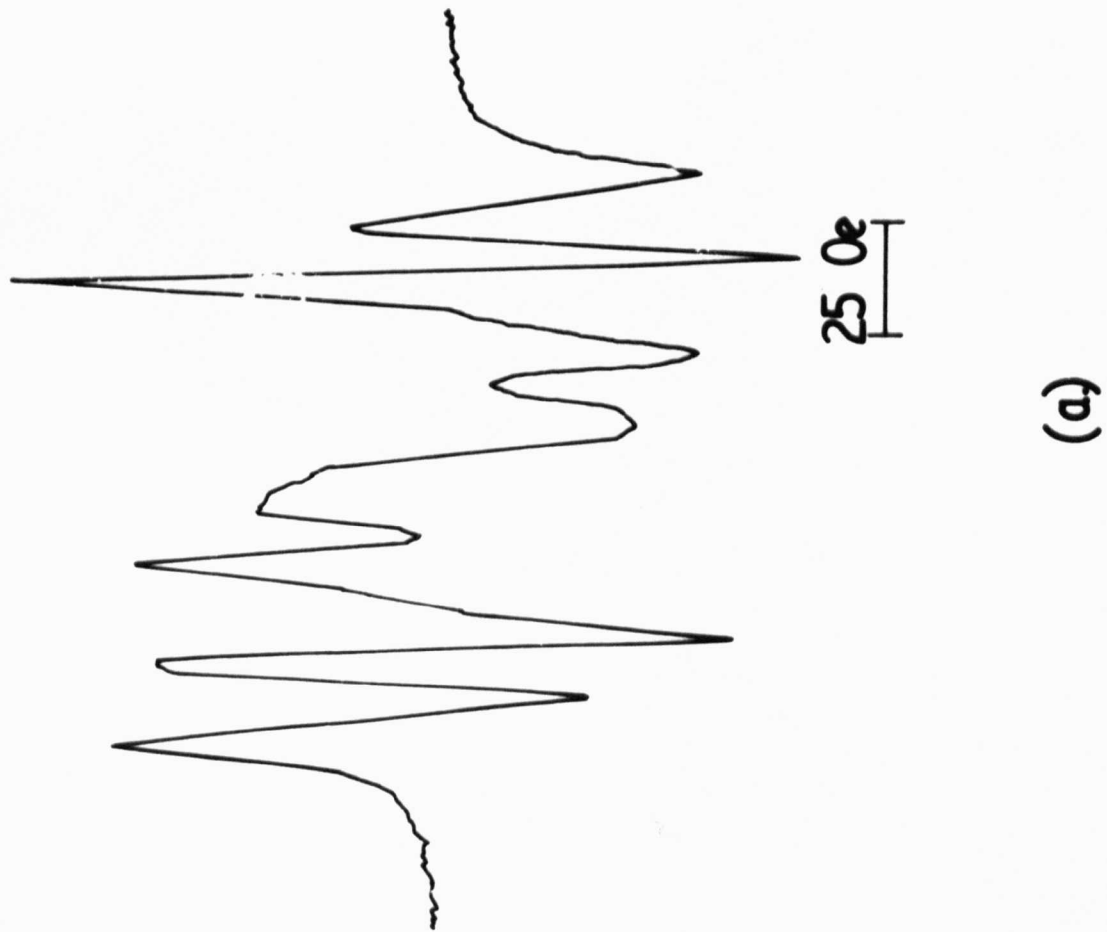
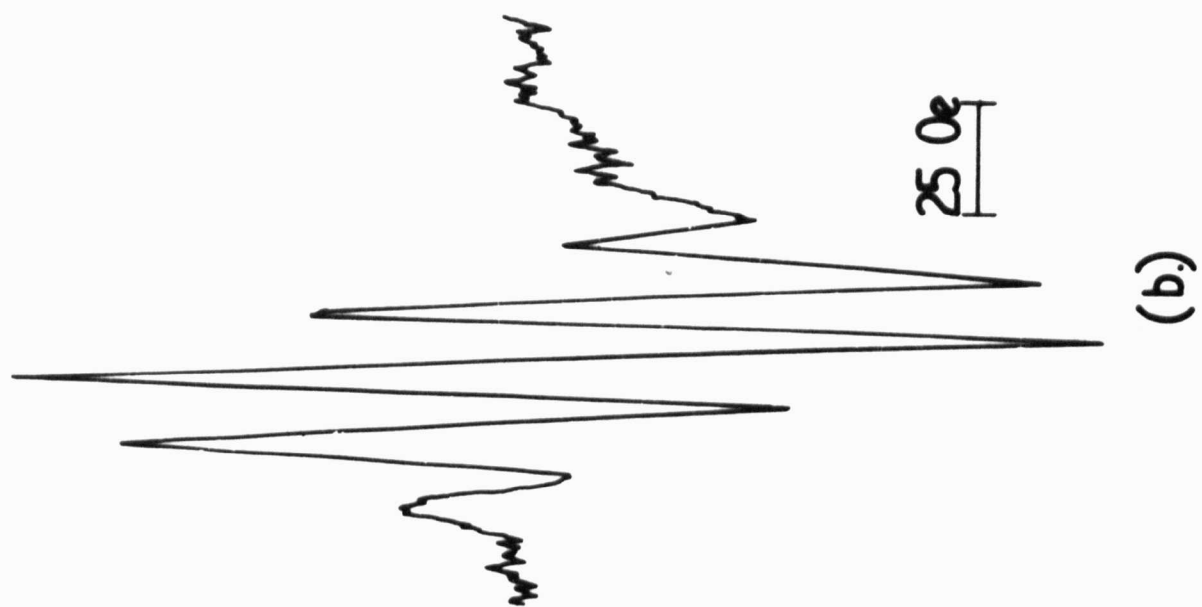


FIGURE 15

**E.S.R. Spectra Obtained During Photo-Oxidation of
Unsaturated Acids by Ce^{IV}**

(a) Acrylic Acid

(b) Vinylacetic Acid



Methacrylic Acid - Photolysis of a solution of methacrylic acid and ceric perchlorate at 77°K produced a large spectrum which, on warming to 120°K , became better resolved and was analysed as the methylvinyl radical with $a_{\text{CH}_3}^{\text{H}} = 19.9$, $a_{\text{H}\beta_1}^{\text{H}} = 57.9$, $a_{\text{H}\beta_2}^{\text{H}} = 32.9$ Oe which compares well with the observed solution spectrum¹⁰⁵ with $a_{\text{CH}_3}^{\text{H}} = 19.48$, $a_{\text{H}\beta_1}^{\text{H}} = 57.89$, $a_{\text{H}\beta_2}^{\text{H}} = 32.92$ Oe. Renewed photolysis and warming to 175°K produced a spectrum attributed to polymethylmethacrylic acid radical characterised by five main lines and four smaller, poorly resolved shoulders, similar in appearance to that obtained from γ -irradiated polymethylmethacrylate.¹⁵⁵ Presumably warming to 175°K effects radical polymerisation by the methylvinyl radical to give the polymethylmethacrylic acid radical $\text{RCH}_2\dot{\text{C}}(\text{CH}_3)\text{CO}_2\text{H}$.

Vinylacetic Acid - Photolysis at 175°K of a solution in 50% methanol and water (v/v) of ceric perchlorate and substrate led to a binomial five-line spectrum with $a_{\text{average}}^{\text{H}} = 14.0$ Oe which was attributed to the allyl radical (fig. 15 (b)). Attempts by other workers to produce a solid state e.s.r. spectrum of the allyl radical by u.v. photolysis of allyl chloride gave instead four peaks of the allenyl radical.¹⁵⁶ A liquid phase allyl radical spectrum was obtained, amongst other species, on electron-irradiation of cyclopropane at 153°K with one proton with $a = 4.06$, two protons with $a = 13.93$ and two protons with $a = 14.83$ Oe.¹⁰⁵

Propiolic Acid - Photolysis at 77°K produced no spectrum, possibly due to radical reactivity even at this temperature. (It is known that $\text{HC}\equiv\text{C}$ is stable at $< 12^{\circ}\text{K}$ ¹³⁵).

4.2.4. Aryl-Substituted Acids

Phenylacetic Acid - Method E yielded a complicated spectrum consisting of signals due to NO_2^{\cdot} and an aromatic radical, identical to that observed during Ce^{IV} photo-oxidations of 2-phenylethanol and 1,2-diphenylethanol and ascribed to the benzyl radical with $a_{\text{CH}_2}^{\text{H}} = 16.5$, $a^{\text{H}} = 5.5$ Oe (three protons).

2-Phenylpropionic Acid - A spectrum similar in general appearance to that of benzyl radical, but wider, was obtained. It is analysed in terms of four equivalent protons with $a_{\text{H}} = 16.5$ Oe and three equivalent protons with $a_{\text{H}} = 5.7$ Oe, and is assigned to $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_3$ radical, the smaller coupling constants referring to approximately equivalent ortho- and para-ring protons.

Other Aryl-substituted Acids - Attempts to generate the styryl and phenyl radicals from cinnamic acid and benzoic acid respectively failed to produce any spectra, and experiments with pyridine carboxylic acids also failed to produce spectra.

4.2.5. Halogen-Substituted Acids

Fluoroacetic Acid - The spectrum at 77°K was broad and complex, but on warming to 175°K the lines became narrower (fig. 16 (a)). The 175°K spectrum is similar to that reported by Fessenden and Schuler for $\dot{\text{C}}\text{H}_2\text{F}$ radical in inert gas matrices,¹⁵⁷ and yields coupling constants of $a_{\text{F}} = 63$, $a_{\text{H}} = 20$ Oe. In a xenon matrix the corresponding values are 64.3 and 21.1 Oe.¹⁵⁷

Trifluoroacetic Acid - A complex spectrum was obtained which became only a little simpler on warming, exhibiting g_{\parallel} and g_{\perp} features with a large hyperfine splitting ca. 200 Oe. Similar spectra have been observed by Adrian, Cochran and Bowers¹⁵⁸ and Loeliger¹⁵⁹ and a theoretical treatment¹⁶⁰ predicts considerable anisotropy of g and A tensors. Accordingly the spectrum was assigned to $\text{CF}_3\dot{\text{C}}$.

Monochloro- and Trichloroacetic Acids - These gave broad spectra displaying insufficient structure to enable worthwhile analysis.

4.2.6. Hydroxy Acids

The thermal reaction between ceric ions and hydroxy acids is normally too fast to enable a sample to be prepared; however, by mixing and subsequently photolysing ceric perchlorate and lactic acid at 273°K, the following results were obtained.

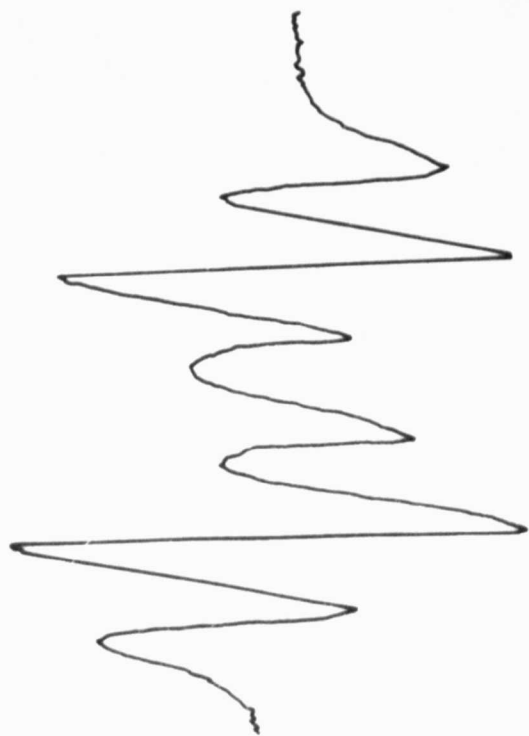
Lactic Acid - At 77°K the spectrum consisted of a mixture of a quartet (1 : 3 : 3 : 1) due to $\text{CH}_3\dot{\text{C}}$ and a five-line spectrum, but on warming to 110°K only the latter signal remained. Its appearance and average coupling of 22.5 Oe (fig. 16 (b)) are in accord with an assignment to the radical $\text{CH}_3\dot{\text{C}}\text{HOH}$, which has been produced in the solid state both by Ce^{IV} (chapter 3) and H_2O_2 photo-oxidations of ethanol.

4.2.7. Dicarboxylic Acids

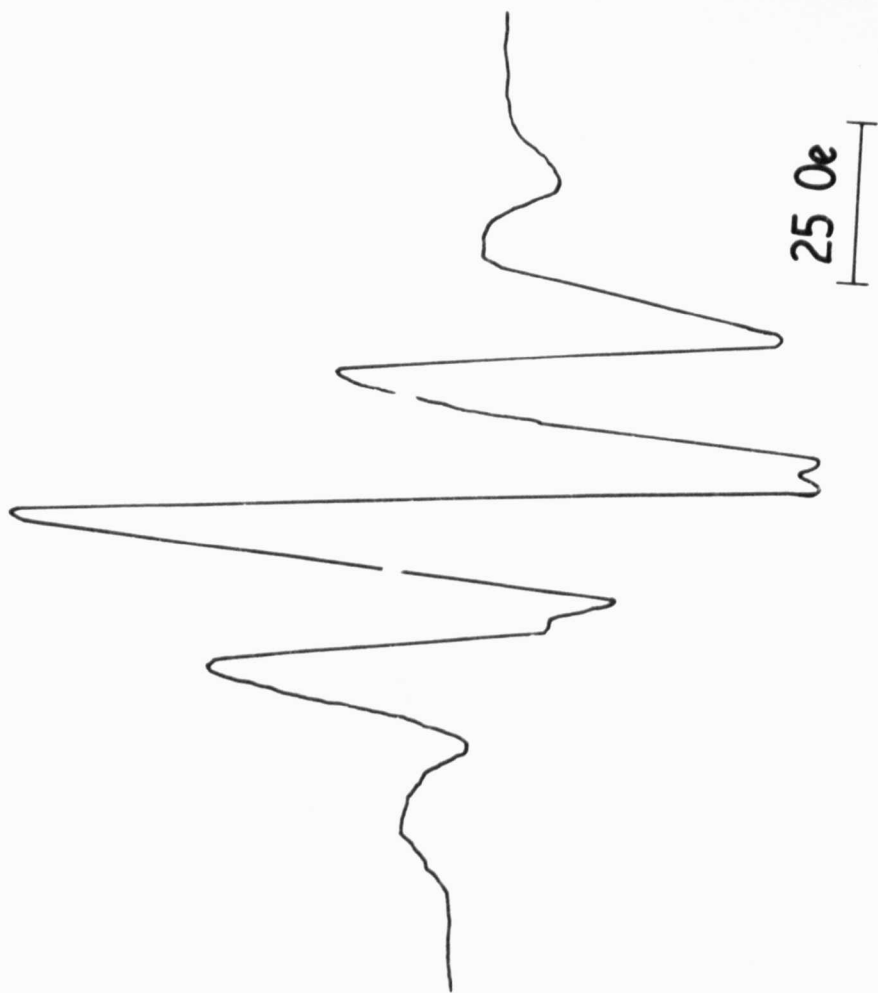
Malonic Acid - The spectrum obtained at temperatures between 77°K and 155°K and shown in figure 17 (a) is identical with that reported by Voerodskil and his colleagues¹⁶¹ for $\text{CH}_2\text{CO}_2\text{H}$ on electron-irradiation of malonic acid at 143°K. Our spectrum yields $a_{\text{H}} = 22.5$ Oe. On warming in the dark to

FIGURE 16

**E.S.R. Spectra Produced During Photo-Oxidation of
(a) Fluoroacetic Acid, (b) Lactic Acid by Ce^{IV}**



(a.)



(b.)

155°K, the spectral intensity increased but at 175°K, the signal decayed rapidly. Renewed photolysis at this temperature, however, produced the quartet of $\text{CH}_3\cdot$. An analogous sequence of events was found for succinic acid and is rationalised in terms of hydrogen atom abstraction from another solute molecule by $\cdot\text{CH}_2\text{CO}_2\text{H}$ to yield $\text{CH}_3\text{CO}_2\text{H}$, which then undergoes photo-oxidation by Ce^{IV} in the second period of irradiation to yield $\text{CH}_3\cdot$ in the manner previously described.

Succinic Acid - A complex sequence of events followed irradiation. The initial spectrum obtained at 77°K, shown in figure 17 (b), displays six lines. On warming to 155°K, this changed to the five-line spectrum shown in figure 17 (c), remaining in the latter form until 175°K when it decayed rapidly in the dark. However, further photolysis of the sample at 175°K produced additional narrower lines with separations corresponding to ethyl radical (fig. 17 (d)). Photolysis of a fresh sample at 175°K produced only the five-line spectrum; however, after some decay of the radical in the dark, further irradiation produced the ethyl radical.

The 77°K spectrum (fig. 17 (b)) was analysed by computer simulation in terms of two equivalent proton hyperfine splittings of 17.4 and one each of 16.0 and 34.0 Oe, whilst the five-line spectrum is due to two equivalent splittings of 17.3 Oe and two further equivalent splittings of 24.0 Oe. This transformation accords with an assignment of both spectra to a single species $\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ which is "locked" in one configuration at 77°K but which begins to exhibit rotation, with a resulting equivalence of the β -protons, at higher temperatures, reproducing exactly the established behaviour of n-propyl radical.¹⁰⁴ The assignments of the coupling constants are:

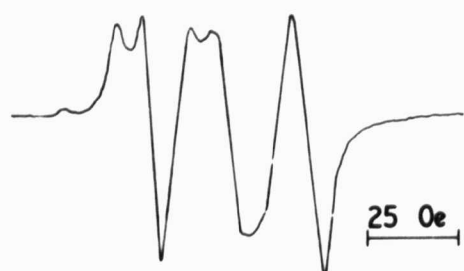
77°K spectrum, i.e. fig. 17 (b); $a_{\text{H}_\alpha} = 17.4$, $a_{\text{H}_{\beta_1}} = 34.0$, $a_{\text{H}_{\beta_2}} = 16.0$ Oe.
 155°K spectrum, i.e. fig. 17 (c); $a_{\text{H}_\alpha} = 17.3$, $a_{\text{H}_\beta} = 24.0$ Oe.

The appearance of the ethyl radical on re-illumination of a pre-irradiated sample at 175°K (after standing for a period in the dark) appears to be associated with the decay of $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$. Sheldon and Kochi⁵⁷ have shown that an important process in the photo-oxidation of $\text{R}\cdot\text{CO}_2\text{H}$ by Ce^{IV} is hydrogen transfer to $\text{R}\cdot$ to give RH , and it seems probable that $\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ decays to give $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ which subsequently undergoes photo-oxidation by

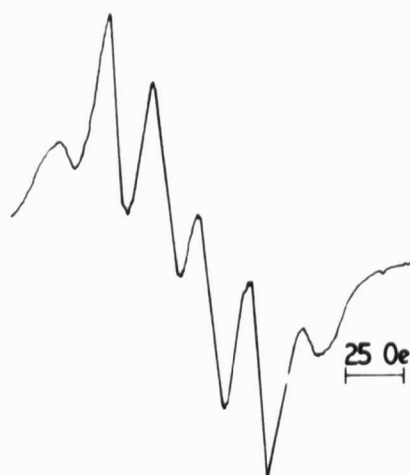
FIGURE 17

**E.S.R. Spectra Obtained During Photo-Oxidation of
Dicarboxylic Acids by Ce^{IV}**

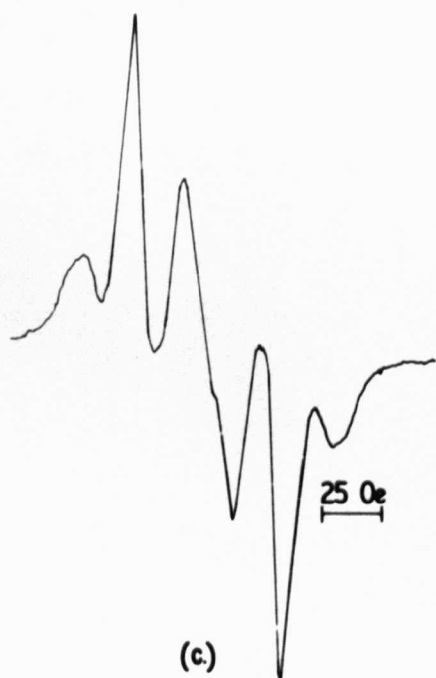
- (a) Malonic Acid at 77°K**
- (b) Succinic Acid at 77°K**
- (c) Succinic Acid following
warming to 155°K**
- (d) Succinic Acid following
irradiation at 77°K , warming
to 175°K and then further
irradiation at 175°K**



(a.)



(b.)



(c.)



(d.)

Ce^{IV} to give C_2H_5 ; the latter process has been shown to occur earlier in this chapter.

1,1-Cyclobutane Dicarboxylic Acid - Photolysis at 77°K produced a five-line spectrum of binomial intensity with $a_{\text{H}} = 32.3$ Oe and is attributed to the 1-cyclobutanecarboxylic acid radical. Warming to 175°K in the dark effected an increase in resolution and further warming caused the radical to decay quickly. Renewal of photolysis at 175°K produced only the five-line spectrum, implying that secondary oxidation of the radical by Ce^{IV} is of a greater importance than hydrogen transfer and subsequent photo-oxidation of the mono-acid.

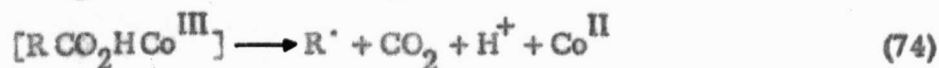
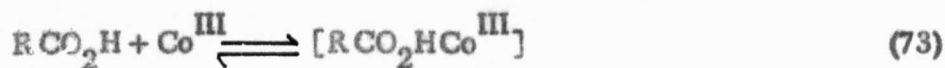
4.2.8. Amino Acids

Glycine - The spectrum illustrated in figure 18 (a) was obtained at 135°K and is similar to that at 77°K except that it is slightly better resolved. It is analysed in terms of coupling from five equivalent protons ($a_{\text{H}} = 18.0$ Oe) and one nitrogen ($a_{\text{N}} = 4.2$ Oe) and a computer simulation based on these figures is given in figure 18 (b). These data suggest an assignment to the species $^+\text{NH}_3 - \text{CH}_2^\cdot$, for which the following coupling constants have been obtained in a crystalline environment at 300°K ¹⁶²; $a_{\text{N}} = 4.1$, $a_{\text{H}\alpha} = 24.7$, $a_{\text{H}\beta} = 19.0$ Oe.

β -Alanine - Photolysis at 77°K produced a six-line spectrum with $a_{\text{H}}^{\text{average}} = 21.1$ Oe, and was assigned to $^+\text{NH}_3\text{CH}_2\text{CH}_2^\cdot$ radical with $a_{\text{H}\alpha} = 21.0$, $a_{\text{H}\beta 1} = 42.0$, $a_{\text{H}\beta 2} = 21.1$ Oe. On warming to 175°K , the six-line spectrum changed to a five-line one, consistent with the onset of free rotation around the C - C bond.

DISCUSSION

Saturated aliphatic acids are, in general, resistant to thermal oxidations by metal ions and are usually only oxidised by metal ions capable of oxidising paraffins, such as Co^{II} ($\text{Co}^{\text{III}} / \text{Co}^{\text{II}} = 1.89$ volts). The mechanism of oxidation by Co^{III} is represented as,¹⁶³

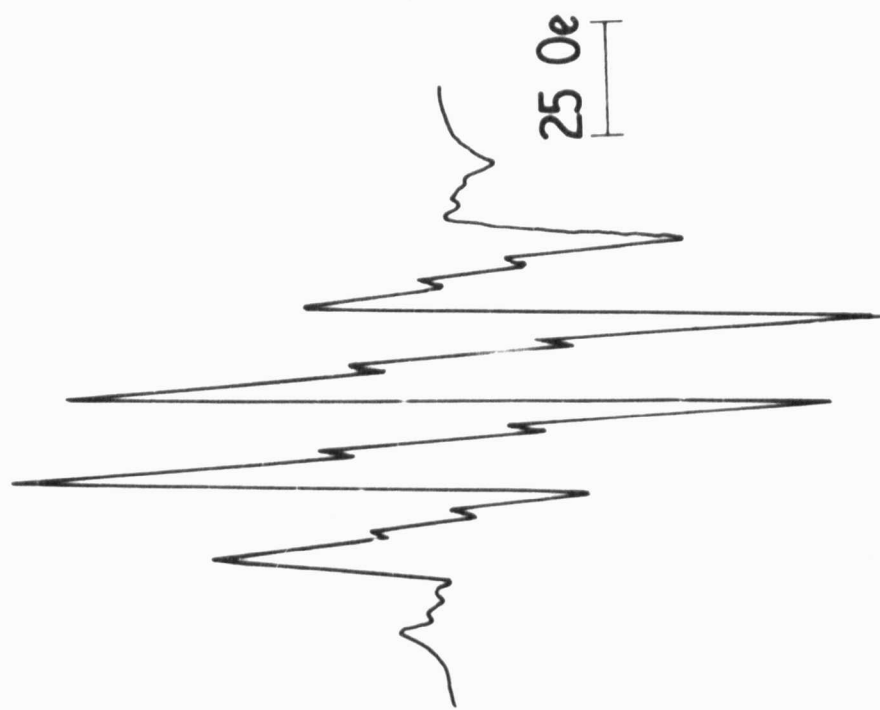


and is based on end-product analysis and the observation of Michaelis-Menten kinetics. The very slow thermal decomposition of acetic acid by Ce^{IV} has been

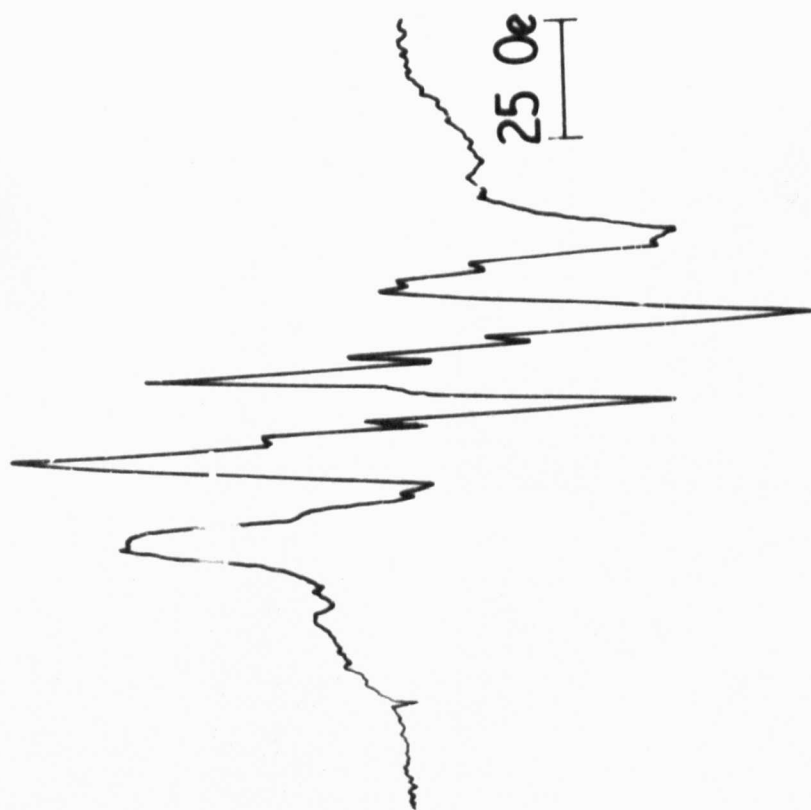
FIGURE 18

**E.S.R. Spectrum Obtained During Photo-Oxidation of
Glycine by Ce^{IV}**

- (a) Experimental**
- (b) Computer Simulation**



(b.)



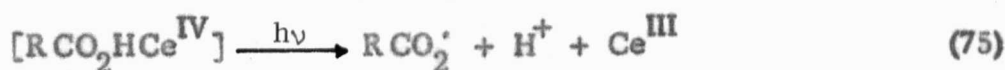
(a.)

studied⁵⁶ and the production of $\text{CH}_3\cdot$ radical proposed.

It is clear from our e.s.r. data with a wide variety of carboxylic acids, that the primary step in the Ce^{IV} photo-oxidation at 77°K is one of oxidative decarboxylation ;



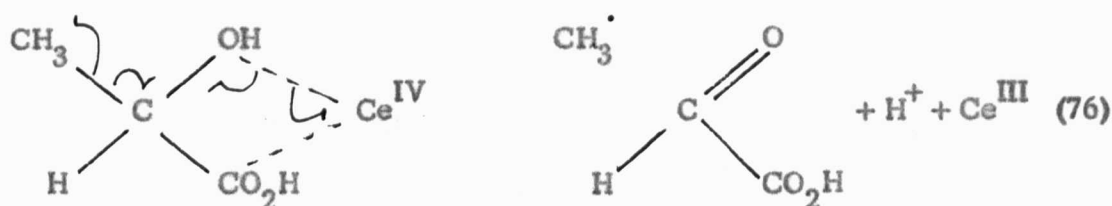
This path is usually dominant and most of the resulting e.s.r. spectra are attributable to a single species with hyperfine coupling corresponding to $\text{R}\cdot$ although there are exceptions. This conclusion accords well with that of Sheldon and Kochi⁵⁷ from product studies, $\text{R}\cdot$ giving both RH (by abstraction) and R^+ (and thence alkenes and esters) from oxidation of $\text{R}\cdot$ by Ce^{IV} . $\phi(\text{CO}_2)$ is uniformly high, reaching 1.11 ± 0.07 and 0.95 ± 0.06 for pivalic acid with Ce^{IV} concentrations of 0.1 and 0.01 M respectively. These authors propose an initial photochemical homolysis,



followed by rapid elimination of CO_2 from the acyloxy radical. However, during our experiments, no e.s.r. evidence was found for $\text{R CO}_2\cdot$ at 77°K even after a few seconds of irradiation followed by immediate determination of the spectrum. Martin's proposed decarboxylation of aliphatic acids by $\text{NO}_3\cdot$ ⁶⁸ during photo-oxidation by ceric ammonium nitrate is discounted on the grounds that (a) no spectrum due to $\text{NO}_3\cdot$ is observed and (b) the results with ceric ammonium nitrate are identical to those using ceric perchlorate, where there is no possibility of $\text{NO}_3\cdot$ formation. The results with Ce^{IV} closely parallel those of Heusler and Loeliger¹⁵² who photolysed carboxylic acid complexes of Pb^{IV} in benzene solution at 77°K , obtaining the corresponding alkyl radical, identified by e.s.r. spectroscopy.

E.s.r. examination of the oxidation of carboxylic acids by $\text{OH}\cdot$ in a flow system indicates mainly a process of H-atom abstraction (although some $\text{CH}_3\cdot$ radicals are observed with acetic acid) and in this manner $\text{OH}\cdot$ and Ce^{IV} behave quite differently.

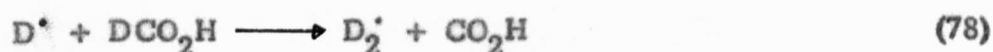
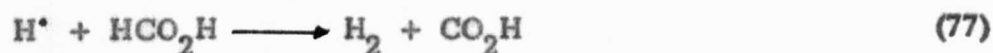
Lactic acid breaks down on photo-oxidation with Ce^{IV} by two pathways, i.e., the "normal" oxidative decarboxylation to give $\text{CH}_3\dot{\text{C}}\text{H}(\text{OH})$ and a fragmentation to give $\text{CH}_3\cdot$.



Such fragmentations are a common feature of Ce^{IV} photo-oxidation of s- and t-alcohols (chapter 3).

Most of the spectra obtained in this chapter are well known. However, those of allyl, cyclopropyl and cyclobutyl may be the first given which are entirely free from absorption by other radicals. Others, for example, of vinyl, which shows at 77°K the eight lines expected of three non-equivalent protons, show an improvement on the literature spectra. The failure of propionic acid to produce ethynyl radical is understandable since this radical has only been observed at 12°K and was shown in chapter 3 to be reactive at 77°K . Spectrum C, obtained during the experiments with HCO_2H and DCO_2H in $\text{H}_2\text{O} + \text{HClO}_4$ and $\text{D}_2\text{O} + \text{DClO}_4$ is probably to be assigned to CO_2H for the following reasons;

- (i) the spectrum is characterised by three g-values and
- (ii) its production on thermal decay of H^\bullet and D^\bullet is in accord with the reactions,



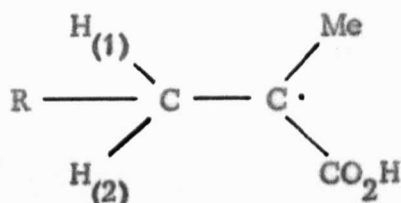
CO_2H has been reported in solution by Norman and West¹⁶⁴ using the $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ oxidation of HCO_2H in a flow system, with $g = 2.002$ and exhibiting a doublet ($a_{\text{H}} = 0.9 \text{ Oe}$) which would certainly not be resolved under our experimental conditions. γ -Irradiation of single crystals of KHCO_3 produces several radicals including one attributed to CO_2H with $g_z = 2.0031$, $g_x = 2.0012$, $g_y = 1.9971$,¹⁶⁵ figures which are close to those reported for CO_2^\bullet .¹⁶⁶ The analysis for spectrum C, due to radicals in an amorphous matrix, gave $g_1 = 2.0052$, $g_2 = 2.0016$, $g_3 = 1.9951$ and is accordingly assigned to CO_2H . The acidic medium ($\sim 4 \text{ M HClO}_4$) used in these experiments precludes the existence of $\text{CO}_2^{\bullet-}$.

The appearance of hyperfine splitting in the peaks for H^\bullet and D^\bullet in an $\text{H}_2\text{O} + \text{HClO}_4$ media (but not $\text{D}_2\text{O} + \text{DClO}_4$ media) indicates some interaction with protons of neighbouring solvent molecules. This phenomenon has also

been observed by Ayscough, Collins and Dainton¹⁶⁷ who found quintet splitting of the H-atom peaks in frozen γ -irradiated 3M sulphuric acid with $a_H \sim 7$ Oe. The diminution of the satellite peak intensities on diluting the solvent with D_2O indicates that the spectra are due to a mixture of "normal" H-atoms and those which are interacting with solvent protons.

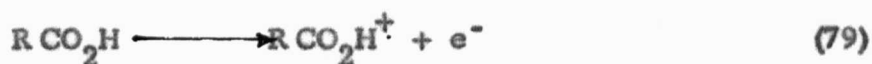
Secondary radical reactions are observed with formic acid, when H^\cdot and D^\cdot , released from the matrix on warming, attack further solute to give \dot{CO}_2H and H_2 and D_2 respectively. The situations with malonic and succinic acids are complicated but have been characterised in the results section. Acetic acid produces some \dot{CH}_2CO_2H by hydrogen abstraction from CH_3CO_2H by CH_3^\cdot , formed initially, in a similar manner to the production of $\dot{CH}_2C(Me)_2OH$ from t-butanol (chapter 3).

The reactions observed with acrylic and methacrylic acid are consistent with initially production of a monomer radical and subsequent thermal reaction on warming to give polymer radicals. The polymethylmethacrylate radical



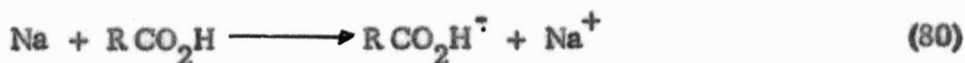
has been analysed completely by Symons¹⁶⁸ further investigation of this radical in the temperature region $245^\circ\text{K} - 280^\circ\text{K}$ by Bamford et al¹⁶⁹ enabled complete resolution of the β -protons and showed them to be slightly inequivalent having splittings of 15.15 and 8.05 Oe and lying at approximately 55° and 65° to the p-orbital of unpaired spin. Limited rotation of these β -protons about the C-C bond axis would lead to selective line broadening and accounts for the low intensities of the shoulder peaks observed in this work. Studies on the polyacrylic radical are not so prolific; however, a solution spectrum of $\text{R}-\text{CH}_2-\dot{\text{C}}\text{H}(\text{CO}_2\text{H})$ has been observed by reaction of OH (from $\text{Ti}^{3+}/\text{H}_2\text{O}_2$) and acrylic acid in a flow system¹⁷⁰ and gives $a_{\text{CH}}^{\text{H}} = 22.62$, $a_{\text{CH}_2}^{\text{H}} = 21.34$ Oe. Analysis of the spectrum, formed upon warming a photolysed sample of Ce^{IV} and acrylic acid to 175°K , yields $a_{\text{CH}}^{\text{H}} = 22.4$, $a_{\text{CH}_2(1)}^{\text{H}} \approx 44.0$, $a_{\text{CH}_2(2)}^{\text{H}} \approx 22.0$ Oe indicating that the radical is locked in one particular conformation, i.e. that with one β -proton lying approximately in the same plane as the unpaired electron orbital.

Electron transfer reactions occur during radiolysis of carboxylic acids ; since many of the carboxylic acids form good crystals, most of the useful information regarding the effects of ionising radiation has been derived from studies of single crystals at room temperature. The radicals produced, formed by loss of an α -H atom and exhibiting considerable anisotropy of the A-tensor, were thought to be the primary species involved in the radiolysis of carboxylic acids. Low-temperature studies,¹⁷¹ however, show that ionisation is the main process, viz.



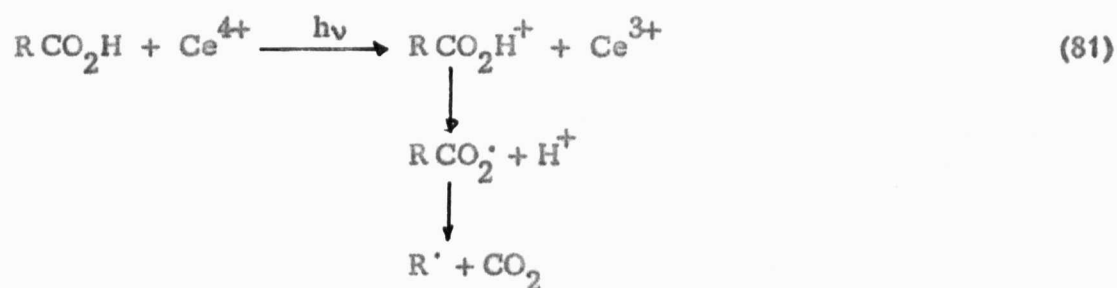
A variety of reactions can now take place, recombination of electron and cation can occur to give a "hot" acid molecule or the electron can react with another acid molecule to give the radical anion $\text{R CO}_2\text{H}^{\cdot-}$. Thus, both radical cations and anions are formed during radiolysis of carboxylic acids.

The reaction between e^- and $\text{R CO}_2\text{H}$ has been studied by Bennett and Gale¹⁷² using the rotating cryostat to deposit sodium atoms in a carboxylic acid matrix at 77°K, to produce $\text{R CO}_2\text{H}^{\cdot-}$, viz.

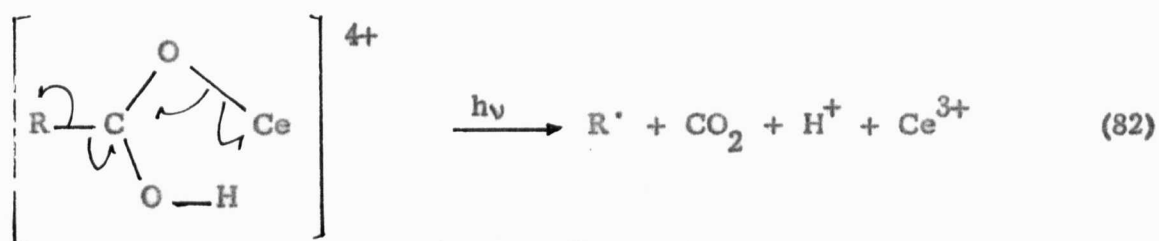


The resulting spectra consisted of a prominent doublet ($a^{\text{H}} \sim 30$ Oe) assigned to a radical configuration in which the carboxylate anion is locked with one proton lying close to the plane defined by the $\text{C}_{\alpha} - \text{C}_{\beta}$ bond and the axis of the orbital containing the unpaired electron. Warming to 140°K effected rotation about this bond and the spectrum changed to a 1:3:3:1 type spectrum ($a_{\text{H}} = 13.05$ Oe) characteristic of interaction between three equivalent protons and the unpaired electron.

Studies on $\text{R CO}_2\text{H}^{\cdot+}$ are not so well documented and direct e.s.r. evidence is lacking; the observation of R^{\cdot} (as well as $\text{R CO}_2\text{H}^{\cdot-}$) during γ -irradiation of carboxylic acids¹⁷¹ and the Ce^{IV} photo-oxidation of the same acid, at cryogenic temperatures, could, however, imply the production of a common intermediate, namely $\text{R CO}_2\text{H}^{\cdot+}$, followed by rapid decomposition even at 77°K to give R^{\cdot} , viz.



It is difficult to differentiate between this mechanism and a concerted process,



Studies at lower temperatures (down to 4.2°K) would probably resolve this dichotomy by stabilising any $\text{R CO}_2\text{H}^+$ formed.

CHAPTER 5

Ce^{IV} PHOTO-OXIDATION OF SOME ORGANIC COMPOUNDS CONTAINING OXYGEN

5. Ce^{IV} PHOTO-OXIDATION OF SOME ORGANIC COMPOUNDS CONTAINING OXYGEN

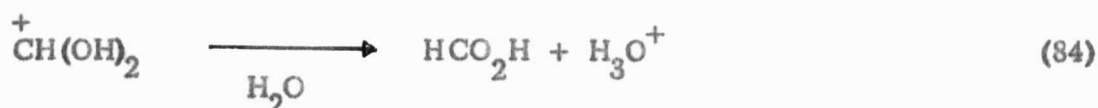
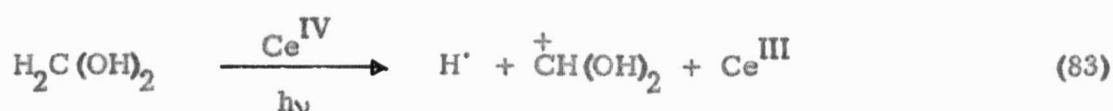
5.1 Introduction

The preceding two chapters have demonstrated the effectiveness of the cryogenic e.s.r. technique to the study of Ce^{IV} photo-oxidations; chapter 3 relates to primary, secondary and tertiary alcohols which are photo-oxidised either by C-H or C-C cleavage processes, the extent of the latter increasing with the degree of alkylation of the hydroxylated carbon atom, whilst chapter 4 shows that in nearly all cases, $\text{R CO}_2\text{H}$ is oxidatively decarboxylated to R^\cdot and most of the primary processes in Ce^{IV} photo-oxidations have been established. In this section a wide variety of organic compounds, namely, aldehydes, ketones, esters and amides have been investigated, together with a very brief study of ethers and an attempt is made to incorporate the results into an overall pattern for Ce^{IV} photo-oxidation of organic substrates. The techniques of sample preparation have been described before (page 29), and for the sake of consistency, sample nomenclature is the same as in the preceding two chapters. Most of the experiments were performed with ceric ammonium nitrate, either neat or in acetonitrile solution and hence, some of the spectra contain the ubiquitous wing peaks of NO_2^\cdot which sometimes distort the spectra and make analysis difficult.

5.2 Results

5.2.1. Aldehydes

Formaldehyde - From both H_2O and D_2O solutions, the spectrum of H-atom ($a_{\text{H}} \sim 500$ Oe) was obtained. In some experiments additional spectra consisting of a singlet centered on $g = 2.0014$ with a peak-to-peak width of ca. 27 Oe and also of formyl radical, were obtained. The origin of the H-atoms is evidently the solute molecules, and C-H fission, with oxidation of the carbon fragment is taking place,



Assignment of the singlet spectrum to CO_2H , shown to be formed in Ce^{IV} oxidation of formic acid (chapter 4) is supported by the g -value but the present spectrum is considerably wider than that found with formic acid. Attempts to prepare a solution of formaldehyde in MeCN failed due to rapid polymerisation.

Acetaldehyde - Method A gave a spectrum consisting mainly of the 1:3:3:1 quartet of methyl radical ($a_{\text{H}} = 22.5$ Oe, $g = 2.0024$) with ca. 10% contribution from a 1:2:1 triplet ($a_{\text{H}} = 20.7$ Oe, $g = 2.0033$). On warming to 135°K in the dark, the signal from CH_3^\cdot diminished, resulting in an increased prominence of the triplet. At 175°K both signals were much weaker but renewed photolysis yielded the same two radicals in about the same proportion found at 77°K. Standing an irradiated sample at 77°K for four hours produced no change in the intensities of the two species. The 1:2:1 triplet spectrum is probably due to an $\text{X}-\text{CH}_2^\cdot$ species, the obvious candidate being CH_2CHO or its hydrated form, $\text{CH}_2\text{CH}(\text{OH})_2$. Livingston and Zeldes¹⁷³ have reported a spectrum believed to be that of CH_2CHO with two principal coupling constants of 19.2 and 18.7 Oe and with $g = 2.0046$, and Buley, Norman and Pritchett¹⁷⁴ are essentially in agreement.

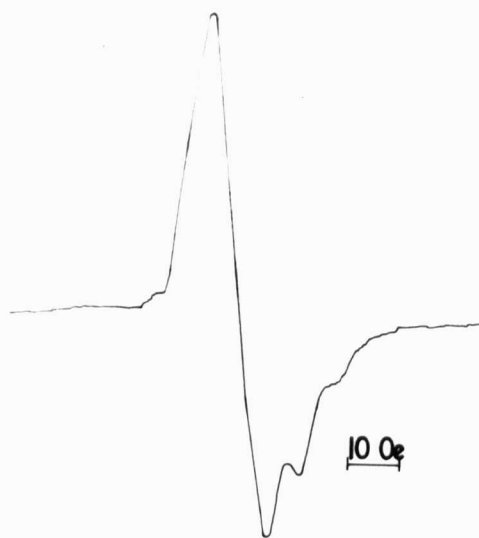
Method C - Brief irradiation produced a basic singlet displaying some structure on the high-field side (fig. 19 (a)) which was analysed in terms of $g_{\parallel} = 1.9949$, $g_{\perp} = 2.0033$, $g_{\text{average}} = 2.0005$ (all ± 0.0005) and is assigned to the acetyl radical on the basis of the similarity with the rather better-resolved spectrum of CH_3CO obtained by Bennett and Mile¹⁷⁵ on mixing acetyl chloride and sodium by means of the rotating cryostat technique (page 14) with $g_{\parallel} = 1.9952$, $g_{\perp} = 2.0034$. Longer periods of irradiation produced, in addition to CH_3CO , signals from CH_3^\cdot and another unidentified species.

Propionaldehyde - Method A yielded a sharp well-resolved spectrum of ethyl radical ($a_{\text{CH}_2} = 21.6$, $a_{\text{CH}_3} = 27.3$ Oe) which remained at temperatures up to 193°K. Method C gave a structureless singlet at 77°K centered on $g = 2.0004$ with a peak-to-peak width of ca. 22 Oe (fig. 19 (b)). Further

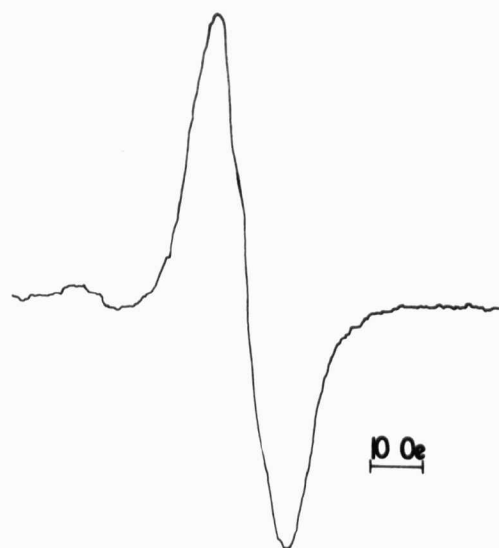
FIGURE 19

**E.S.R. Spectra Obtained During Photo-Oxidation of
Aldehydes by Ce^{IV}**

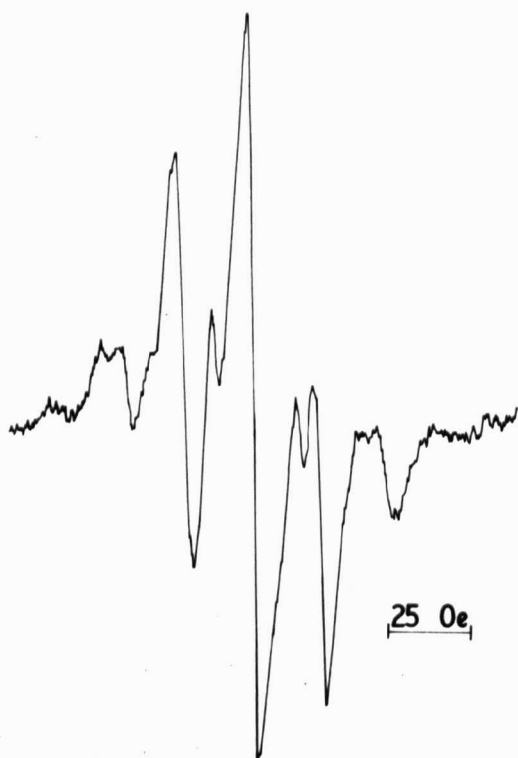
- (a) Acetaldehyde by Method C at 77°K**
- (b) Propionaldehyde by Method C at 77°K**
- (c) Propionaldehyde in CH_3CN photo-oxidised by ceric ammonium nitrate at 77°K followed by warming to 120°K**
- (d) Crotonaldehyde with ceric ammonium nitrate in CH_3CN at 77°K**



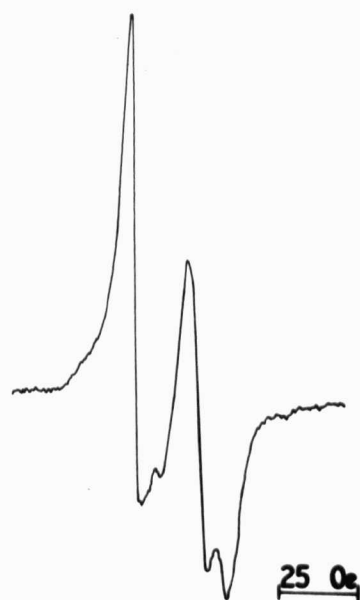
(a)



(b)



(c)



(d)

irradiation at 77°K produced a new sharp peak which appeared to low field of the singlet. Irradiation at 100°K gave, in addition, a sharp peak to high field (as well as low field) of the singlet, the sharp peaks being separated by 26.2 Oe. These suggest the presence of ethyl radical and further irradiation produced the other absorption lines of this radical. The low g -factor of the singlet is compatible with an assignment to $\text{C}_2\text{H}_5\dot{\text{C}}\text{O}$. Radiolysis of $\text{C}_2\text{H}_5\text{COCl}$ in a 3-methyl pentane glass at 77°K produced a singlet of width 15 Oe attributed also to $\text{C}_2\text{H}_5\dot{\text{C}}\text{O}$ radical.¹⁷⁶

Solutions of ceric ammonium nitrate and propionaldehyde in CH_3CN gave the same singlet described above at 77°K but on standing in the dark at 120°K , the singlet disappeared, giving way to a new spectrum of five lines with an approximately binomial intensity distribution ($a_{\text{H}} = 20.4$ Oe, $g = 2.0033$) together with a small absorption due to $\text{C}_2\text{H}_5\dot{\text{C}}\text{O}$. The five-line spectrum is probably due to $\text{CH}_3\dot{\text{C}}\text{HCHO}$ formed either by abstraction of an α -H atom from substrate by $\text{C}_2\text{H}_5\dot{\text{C}}\text{O}$ or by isomerisation of the latter radical.

Crotonaldehyde - A solution of the latter in CH_3CN with ceric ammonium nitrate underwent photo-irradiation to give the spectrum shown in fig. 19 (d) which was analysed in terms of $g_{\parallel} = 1.9914$, $a_{\parallel} = 8.7 \pm 0.5$ Oe, $g_{\perp} = 2.0046$, $a_{\perp} = 9.3 \pm 0.5$ Oe. The low g -factor suggests an assignment to the acyl radical $\text{CH}_3\text{CH}=\dot{\text{C}}\text{HO}$. Photolysis of a fresh sample at 175°K showed a four-line spectrum with $a_{\text{H}} = 12.3 \pm 0.5$ Oe, typical of the allyl-type radicals observed from allyl alcohols (chapter 3) and allylic acids (chapter 4) and is assigned to the radical $\dot{\text{C}}\text{H}_2-\text{CH}=\text{CH}-\text{CHO} \rightleftharpoons \text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}-\text{CHO}$. Cooling to 77°K produced only an increase in line width and re-photolysis at this temperature resulted in a distortion of the spectrum due to the appearance of the acyl-type radical $\text{CH}_3-\text{CH}=\dot{\text{C}}\text{HO}$.

Benzaldehyde - Method C gave a singlet with $g_{\parallel} = 1.9956$, $g_{\perp} = 2.0023$. The g -factor and lack of any observable hyperfine splitting suggests an acyl radical, i.e. benzoyl radical, $\text{Ph}\dot{\text{C}}\text{O}$, for which the (averaged) g -factor in solution is 2.0014, and in the solid state 2.0008. The hyperfine coupling from the meta-protons of 1.16 Oe found in solution would not be observed under solid-state conditions.

Phenyl Acetaldehyde - Method C yielded at 77°K a spectrum analysed

as benzyl by comparison with other solid-state spectra (page 35) together with an underlying singlet assigned to $C_6H_5CH_2\dot{C}O$ of width approximately 20 Oe. These results are explained in the discussion section.

5.2.2. Ketones

Acetone - Method A yielded initially a composite spectrum consisting mostly of the quartet of $CH_3\dot{C}$ with a minor 1:2:1 triplet, but further irradiation produced an enhancement of the latter, which maintained a distorted appearance, with $a_H = 21.1$ Oe and $g = 2.0031$ (fig. 20 (a)). Warming to $175^\circ K$ resulted in loss of the triplet spectrum and $CH_3\dot{C}$ finally disappeared at $200^\circ K$ (even under irradiation). Method C produced the same 1:2:1 triplet together with signals from $CH_3\dot{C}$ and $NO_2\dot{C}$. The triplet originates from a species of type $X-CH_2\dot{C}$, probably $CH_3COCH_2\dot{C}$ for which $a_H = 19.5 \pm 0.3$, $a_{CH_3} = 0.95 \pm 0.07$ Oe and $g = 2.0042$ in solution.¹⁷⁴

Methyl Ethyl Ketone - Method A produced a mixture of spectra due to $CH_3\dot{C}$ and a five-line spectrum of binomial character with $a_H = 20.6$ Oe and $g = 2.0030$. On warming to $115^\circ K$ the contribution due to $CH_3\dot{C}$ became very small (fig. 20 (b)) and the five-line signal remained until $175^\circ K$. Method C gave solely the five-line spectrum ($a_H = 21.1$ Oe, $g = 2.0037$) which is probably due to the four approximately equivalent protons in $CH_3CO\dot{C}HCH_3$.

Diethyl Ketone - Method A gave a radical mixture, namely, a binomial five-line spectrum ($a_H = 20.5$ Oe, $g = 2.0033$) closely similar to that obtained with methylethyl ketone and attributed to $CH_3\dot{C}HCO\dot{C}_2H_5$ together with peaks due to $C_2H_5\dot{C}$ (fig. 20 (c)). Method C gave only the five-line spectrum ($a_H = 20.8$ Oe). (Both methylethyl ketone and diethyl ketone gave similar five-line spectra following high-energy irradiation).¹³²

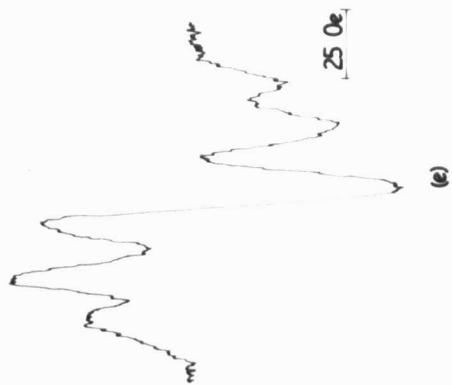
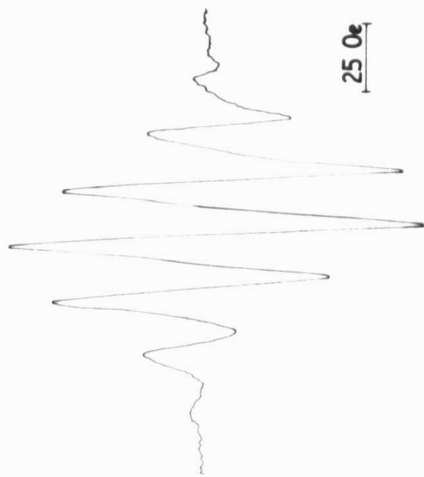
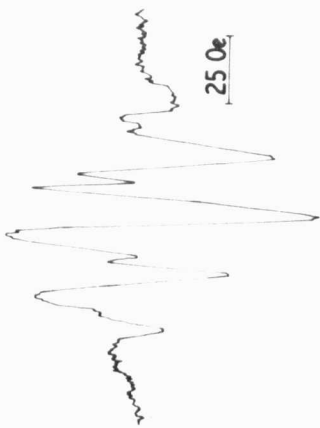
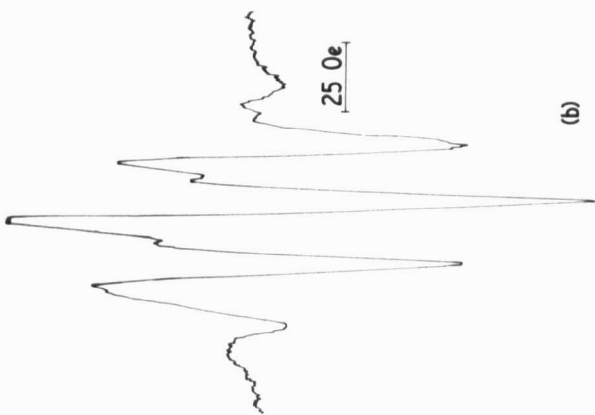
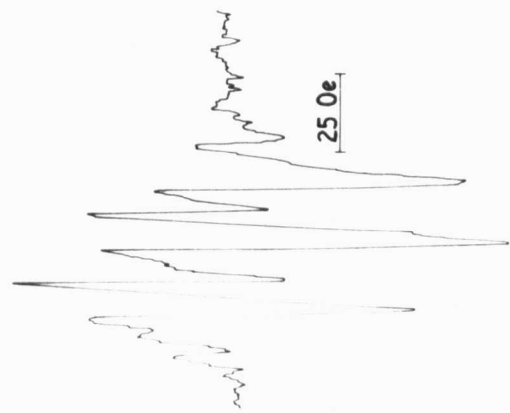
Methylisopropyl Ketone - Method C produced the approximately binomial seven-line spectrum with $a_H = 19.9$ Oe and $g = 2.0038$ shown in figure 20 (d). This corresponds to coupling from six equivalent protons, presumably from the radical $(CH_3)_2\dot{C}COCH_3$.

Di-isopropyl Ketone - Method C gave a mixture of spectra due to $NO_2\dot{C}$ and a seven-line binomial spectrum of which one line was 'lost' under an absorption line of $NO_2\dot{C}$. The binomial spectrum gave $a_H = 19.6$ Oe and $g = 2.0040$ and it disappeared on warming to $178^\circ K$. A CH_3CN solution of oxidant and substrate gave the same seven-line spectrum but in smaller quantity. The radical

FIGURE 20

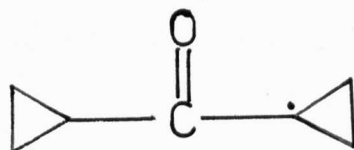
**E.S.R. Spectra Obtained During Photo-Oxidation of
Ketones by Ce^{IV}**

- (a) Acetone by Method A at 77°K**
- (b) Methyl ethyl Ketone by Method A at 115°K**
- (c) Diethyl Ketone by Method A at 77°K**
- (d) Methyl isopropyl Ketone by Method C
at 77°K**
- (e) Dicyclopropyl Ketone in CH_3CN photo-
oxidised by ceric ammonium nitrate at
 77°K followed by warming to 175°K**



responsible is presumably $(\text{CH}_3)_2\text{C} \cdot \text{CO} \text{CH}(\text{CH}_3)_2$.

Dicyclopentyl Ketone - Photo-irradiation by method C and also of CH_3CN solutions of substrate and ceric ammonium nitrate gave, at 77°K , both a broad, five-line spectrum and NO_2^\cdot , but the latter disappeared on warming to 175°K , leaving the five-line species with rather more highly resolved lines shown in figure 20 (e) ($a_{\text{H}} = 20.0 \text{ Oe}$) which originates from the radical



Cyclopentanone Cyclohexanone - Photo-irradiation of solutions in CH_3CN with ceric ammonium nitrate gave quite intense and highly reproducible spectra of some complexity, showing some anisotropic effects and it was thought that a possible mixture of radicals was involved. However, attempts to selectively remove one of the contributing species by controlled warming to various temperatures were unsuccessful in all cases, the ratios of the line intensities staying constant.

5.2.3. Esters

Methyl Acetate - Whilst method A gave only CH_3^\cdot at 77°K , method C gave a 1:2:1 triplet ($a_{\text{H}} = 21 \pm 1 \text{ Oe}$) and NO_2^\cdot , and solutions of substrate and ceric ammonium nitrate in CH_3CN gave CH_3^\cdot , NO_2^\cdot and the 1:2:1 triplet ($a_{\text{H}} = 21 \pm 1 \text{ Oe}$) but CH_3^\cdot decayed rapidly at 100°K . The 1:2:1 triplet originates from an $\text{X} - \text{CH}_2^\cdot$ species of which $\text{CH}_2\text{CO}_2\text{CH}_3$ seems the most likely in view of the site of attack in other esters (see below), although a similar pattern would be expected from $\text{CH}_3\text{CO}_2\text{CH}_2^\cdot$. (In aqueous solution $\text{CH}_2\text{CO}_2\text{CH}_2^\cdot$ and $\text{CH}_3\text{CO}_2\text{CH}_2^\cdot$ are reported to give coupling constants of 21.8^{111} and $20.3^{177} \pm 0.4 \text{ Oe}$ respectively).

Ethyl Acetate - Method A gave only a sharp spectrum of CH_3^\cdot , whilst method C and a solution of the reactants in CH_3CN gave, in addition, a 1:2:1 triplet with $a_{\text{H}} = 22 \pm 1 \text{ Oe}$ which is attributed to $\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ because attack on the ethyl group would have produced an approximately binomial five-line spectrum in view of the known solution spectra¹⁷⁷ of $\text{CH}_3\text{CO}_2\dot{\text{C}}\text{HCH}_3$ and $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2^\cdot$.

Methyl Propionate - CH_3CN solutions of substrate and ceric ammonium nitrate gave, on irradiation, a binomial five-line spectrum ($a_{\text{H}} = 25.4 \text{ Oe}$) plus NO_2^\cdot radical, but method C gave the five-line spectrum only. This probably arises from the coupling of four approximately equivalent protons in $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{CH}_3$, which has been characterised in solution with $a_{\text{CH}}^{\text{H}} = 20.3 \pm 0.3$, $a_{\text{CH}_3}^{\text{H}} = 24.9 \pm 0.6 \text{ Oe}$.¹⁷⁷

Isopropyl Isobutyrate - Photolysis of a CH_3CN solution of substrate and ceric ammonium nitrate yielded a spectrum indicating a mixture of radicals at 77°K . Warming the sample to 113°K resulted in the disappearance of one species, leaving the seven-line spectrum ($a_{\text{H}} = 20.8 \text{ Oe}$, $g = 2.0027$) shown in figure 21(a), which is attributed to the radical $(\text{CH}_3)_2\dot{\text{C}}\text{CO}_2\text{CH}(\text{CH}_3)_2$.

Ethyl Cyanoacetate - Irradiation by method C gave NO_2 and an unambiguous spectrum of $\dot{\text{C}}\text{H}_2\text{CN}$ identical to that observed in the preceding chapters and to that published by Svejda and Volman from photolysis of CH_3CN with light of $\lambda = 185 \text{ nm}$.¹⁷⁸

Ethyl Phenylacetate - Photo-oxidation in CH_3CN by ceric ammonium nitrate gave a broad spectrum which became better-resolved on warming, e.g. that in figure 21(b) was recorded at 133°K . It was analysed in terms of coupling from three approximately equivalent protons ($a_{\text{H}} = 6.2 \text{ Oe}$) and a single proton ($a_{\text{H}} = 15.2 \text{ Oe}$) and the corresponding computer simulation gave an identical appearance. This distribution of spin densities suggests a benzyl-type radical, $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCO}_2\text{C}_2\text{H}_5$, with near-equivalence of the ortho- and para-ring protons and a large spin density at the benzylic proton.

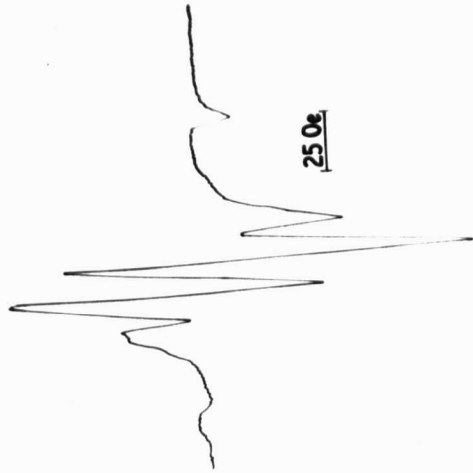
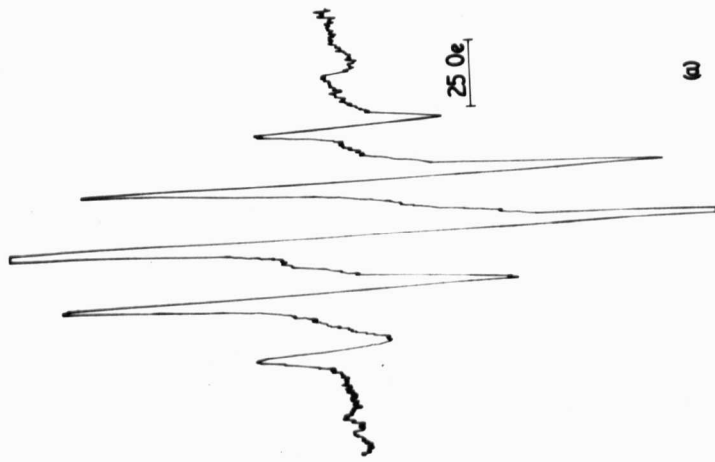
Methyl and Ethyl Crotonates - Photo-oxidation in CH_3CN solution by ceric ammonium nitrate produced similar e.s.r. spectra in these two cases, consisting of NO_2^\cdot and a four-line spectrum (fig. 21(c)) with $a_{\text{H}} = 12.3 \text{ Oe}$ (methyl ester) and $a_{\text{H}} = 13.7 \text{ Oe}$ (ethyl ester) and $g = 2.0027$. The coupling constants and the general appearance of the spectra, suggests an assignment to the allyl-type radicals, $\dot{\text{C}}\text{H}_2 - \text{CH} = \text{CH} - \text{CO}_2\text{R} \rightleftharpoons \text{CH}_2 = \text{CH} - \dot{\text{C}}\text{HCO}_2\text{R}$ ($\text{R} = \text{Me}$ or Et).

Methyl Methacrylate - Irradiation in the presence of ceric ammonium nitrate in CH_3CN solution gave a broad, approximately binomial five-line spectrum ($a_{\text{H}} = 23 \text{ Oe}$) shown in figure 21(d) which, on warming to 175°K , gave,

FIGURE 21

E.S.R. Spectra Obtained During Photo-Oxidation of
Esters in CH_3CN Solution by Ceric Ammonium Nitrate

- (a) Isopropyl Isobutyrate photo-oxidised
at 77°K followed by warming to 113°K
- (b) Ethylphenylacetate photo-oxidised at
 77°K followed by warming to 133°K
- (c) Ethylcrotonate at 77°K
- (d) Methylmethacrylate at 77°K
- (e) Methylmethacrylate photo-oxidised
at 77°K followed by warming to 175°K
(the arrows indicate the four new lines
appearing at the higher temperature
referred to in the text)



in addition to five now well-resolved peaks ($a_H = 23.2$ Oe) at the same field positions as those found at 77°K , four additional peaks with $a_H = 23.1$ Oe (fig. 21 (e)). Recooling the sample to 77°K resulted in no apparent change, but re-illumination at 77°K produced a further specific enhancement of the initial five-line spectrum. This sequence suggests the following processes :

- (a) irradiation at 77°K gives the monomeric, vinylic radical $\cdot\text{CH}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ (the alternative allylic radical, $\text{CH}_2=\dot{\text{C}}(\text{CO}_2\text{CH}_3)-\text{CH}_2\cdot$ would be expected to show a coupling constant of ca. 13 ± 1 Oe),
- (b) warming to 175°K effects radical polymerisation by the vinylic radical to give the polymethyl methacrylate radical $\sim\text{CH}_2\dot{\text{C}}(\text{CH}_3)\text{CO}_2\text{CH}_3$ which is known from several solid state studies¹⁷⁹ to display a total of nine lines, comprising five principal lines ($a_H = 23.0$ Oe) interspersed with four less intense lines. The precise pattern is reproduced in figure 21 (e).
- (c) recooling the sample to 77°K leaves the nine-line spectrum unaltered (in particular, the five main peaks do not become broadened as in figure 21(d)), whilst re-irradiation introduces fresh radicals of the original, broad vinylic type, the five lines of which coincide with those of the five, narrow, principal lines of the polymethyl methacrylate radical.

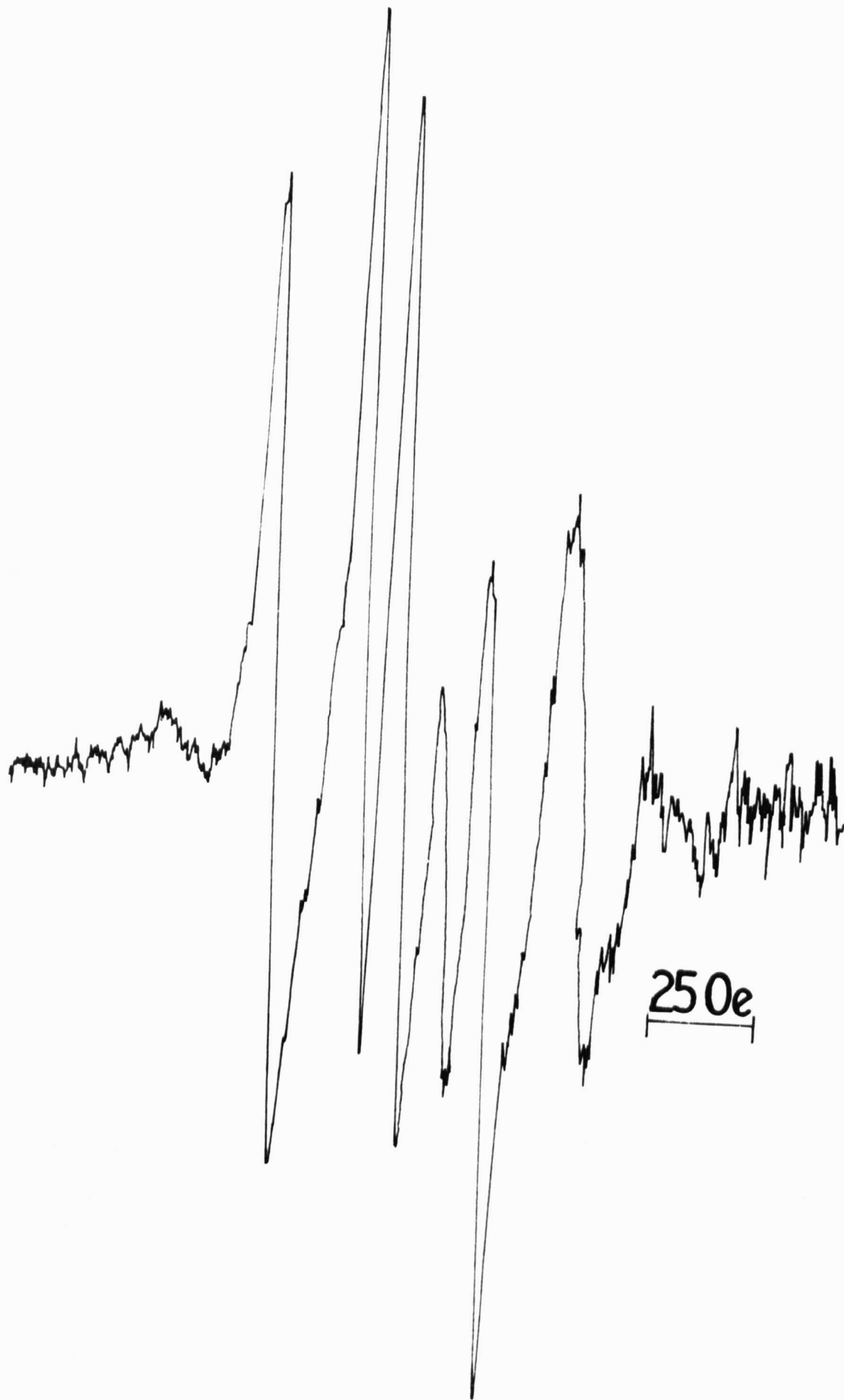
Ethyl Trichloroacetate . - Examination by method C produced a poor spectrum with insufficient resolution to allow a worthwhile and meaningful analysis.

5.2.4. Amides

Formamide - Method C gave a spectrum at 77°K consisting of $\text{NO}_2\cdot$ and a second radical, but the latter alone persisted at 175°K (fig. 22). It was analysed in terms of one proton ($a_H = 30.0$ Oe) and one nitrogen atom ($a_N = 22.0$ Oe). The similarity of these values with those published for the $\cdot\text{CONH}_2$ radical, obtained by direct photolysis of formamide, i.e. $a_H = 31$, $a_N = 22$ Oe, indicates that this is the species generated in the photo-oxidation. The lack of observable

FIGURE 22

E.S.R. Spectrum of $\cdot\text{CONH}_2$ Obtained by Method C



coupling from the second amide proton is due to restricted rotation about the C-N bond. Livingston and Zeldes¹⁸⁰ report the coupling from the second proton to be 1.27 Oe at 300°K in solution during the acetone-sensitised photo-decomposition of formamide whilst Smith and Wood¹⁸¹ obtain a similar value in the oxidation by the Ti^{3+}/H_2O_2 couple, which they proposed as $HCONH\cdot$, and this problem will be reviewed in the discussion section of this chapter.

N,N-Dimethylformamide - Method C yielded a large 1:2:1 triplet with $a_H = 19.1$ Oe and is attributed to an $R-CH_2\cdot$ species of which the most likely candidate is $HCON(Me)CH_2\cdot$. Radiation damage in irradiated N-alkyl substituted amides¹⁸² results in the loss of a proton from the carbon atom of the alkyl group adjacent to nitrogen and a similar process is clearly occurring during Ce^{IV} photo-oxidations.

Acetamide - Method A yielded $CH_3\cdot$ ($a_H = 22.8$ Oe) at 77°K. Examination by method E yielded at 77°K a mixture of $CH_3\cdot$ and a 1:2:1 triplet ($a_H = 23.1$ Oe). Warming to 175°K in the dark effected a decrease in $CH_3\cdot$ leaving as the main component the triplet species. Photolysis of a fresh sample at 175°K gave only the triplet species ($a_H = 23.0$ Oe). The triplet presumably originates from an $RCH_2\cdot$ species of which the most likely species is $\dot{C}H_2CONH_2$ formed either by $CH_3\cdot$ attack on acetamide or by H-abstraction by Ce^{IV} .

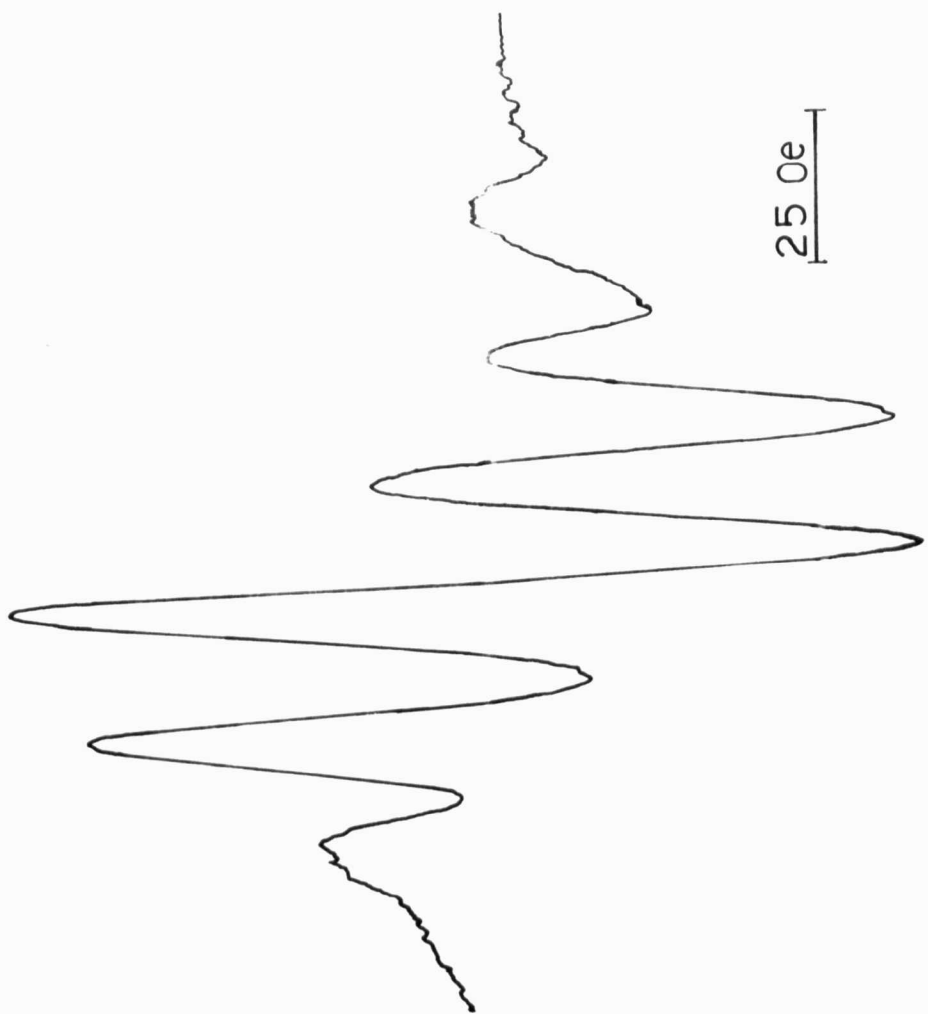
5.2.5. Ethers

Diethyl Ether - Photolysis by method A at 77°K produced a mixture of radicals consisting of a sharp quartet of 1:3:3:1 intensity distribution with $a_H = 22.8$ Oe assigned to $CH_3\cdot$ and a five-line spectrum of approximate binomial intensity with $a_H = 21.0 \pm 1.0$ Oe probably arising from $CH_3\dot{C}HOC_2H_5$ radical where α - and β -protons are nearly equivalent. Method C, and also an acetonitrile solution of ceric ammonium nitrate and diethyl ether, gave a five-line spectrum shown in figure 23 (a), and $NO_2\cdot$ with $a_H = 19.8 \pm 0.3$ Oe. Warming this sample in the dark had little effect on the resolution and the signal decayed completely at 175°K. A solution spectrum of $CH_3CHOC_2H_5$ formed by oxidation with the Ti^{3+}/H_2O_2 couple¹¹¹ gives $a_H^\alpha = 13.8$, $a_H^\beta = 21.5$ Oe.

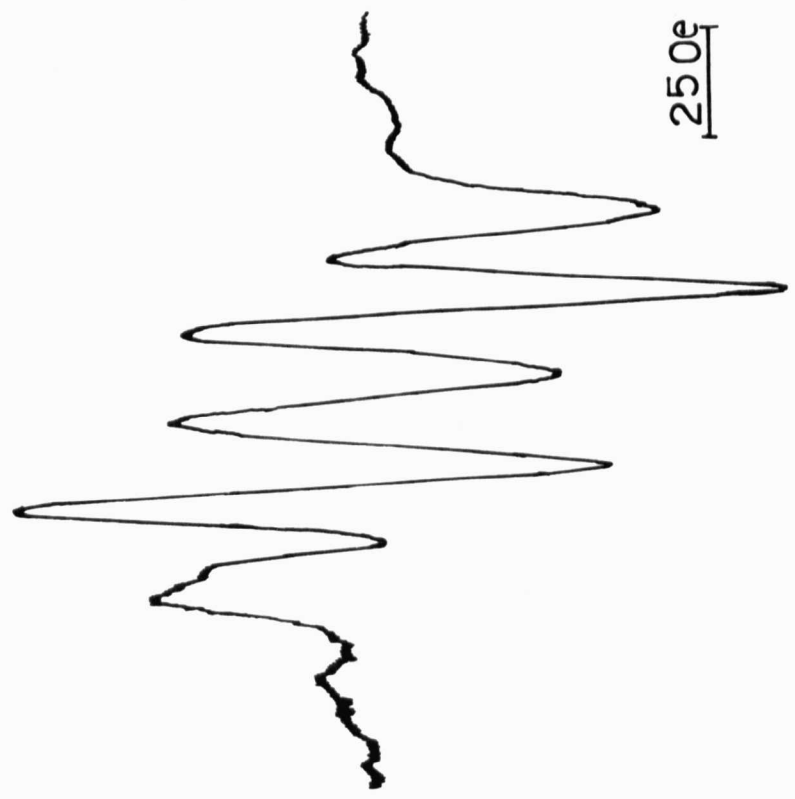
Tetrahydrofuran - Examination by method A at 77°K yields a five-line spectrum shown in fig. 23 (b), and analysed in terms of splitting from two protons of approximately 18.0 Oe and one proton of 39 Oe and is assigned to the

FIGURE 23

E.S.R. Spectra Produced by Photo-Oxidation by
 Ce^{IV} of (a) Diethylether, (b) T.H.F.

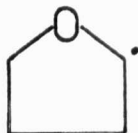


(a)



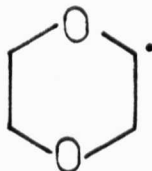
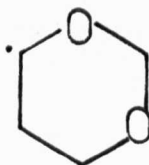
(b)

α -tetrahydrofuran radical with the two inequivalent β -protons presumably locked



into a particular configuration at 77°K. A similar sample using ceric ammonium nitrate in the neat ether produced an identical spectrum, together with some peaks due to NO_2^\cdot . Solution studies of this radical give $a_\alpha^{\text{H}} = 12.4$, $a_\beta^{\text{H}} = 28.2$ Oe with γ -coupling < 2.0 Oe.¹⁸³ The average coupling of the β -protons observed in the solid state is 28.5 Oe, in reasonable agreement with the solution values.

Dioxans - Both 1,3 and 1,4 dioxan gave poorly resolved spectra displaying insufficient structure to enable analysis; however, measurement of the g -value¹⁸³ (2.0031 ± 0.0003) indicates that the radicals observed are probably those formed by α -H abstraction to give



respectively.

Diisopropyl ether, Diallyl ether - The preparation of samples with sufficient Ce^{IV} concentration proved impossible and precluded these ethers from further study by this method.

DISCUSSION

As in the previous two chapters, the Ce^{IV} photo-oxidations of the organic molecules examined appear to be remarkably 'clean', i.e. many substrates are photo-oxidised to a single free radical and the remainder to two at most. This situation is simpler than that encountered during direct u.v. photolysis of certain of the substrates, for example, formamide, when several modes of fission operate¹⁸⁴ or when photolysis products are more strongly absorbing, or break down with a higher quantum yield than the starting molecule. The specificity found in these experiments results in part from the use of light of $\lambda > 300$ nm which restricts photochemical events to the various Ce^{IV} species.

From the earlier studies and from complementary product analysis and

quantum yield results of Sheldon and Kochi on the Ce^{IV} photo-oxidation of carboxylic acids,⁵⁷ it appears that three main modes of photo-oxidation exist, namely,

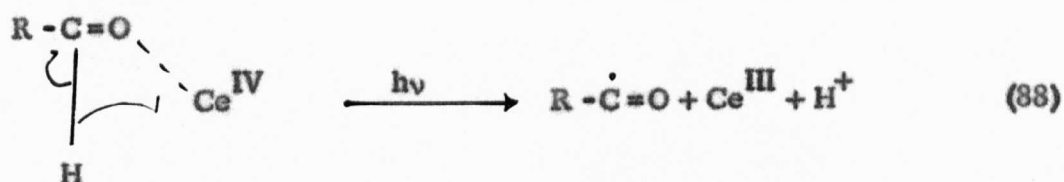


Reactions are usually completed by oxidation of R^\cdot by a second Ce^{IV} species to R^+ which is hydrolysed to ROH , although a considerable variety of secondary reactions of R^\cdot have been characterised.

All three modes are important with the set of substrates examined in the present chapter.

Aldehydes

In all cases using either method (Ce^{IV} dissolved in neat organic liquid or solutions of oxidant and substrate in CH_3CN), C-H fission occurs to give the corresponding acyl radical with its characteristic, predominantly singlet character and low g-value ($g \sim 2.0004$) and exhibiting only weak coupling from hydrogen atoms in the group R,



Some of the acyl radicals produced show thermal and photochemical reactions. Thermal reactions are observed with propionyl and crotonyl radicals on warming in the dark to give $\text{CH}_3\dot{\text{C}}\text{HCHO}$ and $\text{CH}_3-\text{CH}_2=\dot{\text{C}}\text{HCHO}$ at 120° and 175°K respectively, by an intramolecular (isomerisation) process or an intermolecular (abstraction of an α -H atom from the substrate) process. Photochemical reactions of $\text{R}\dot{\text{C}}\text{O}$ are observed when $\text{R}\dot{\text{C}}\text{O}$ is subjected to prolonged irradiation with $\lambda > 300 \text{ nm}$ to give R^\cdot and CO ; this form of reaction is observed with acetyl and propionyl to give CH_3^\cdot and $\text{C}_2\text{H}_5^\cdot$ respectively. The production of benzyl radical at 77°K as the main component in the photo-oxidation of phenylacetaldehyde implies extreme photosensitivity of $\text{C}_6\text{H}_5\text{CH}_2\dot{\text{C}}\text{O}$ radical in the region $\lambda > 300 \text{ nm}$. Benzoyl and crotonyl radicals are resistant to this form of photochemical behaviour

consistent with the findings of Noda, Fueki and Kuri who observed that acyl radicals having a conjugated system next to the carbonyl group were rendered inert to photochemical rearrangements.¹⁸⁵

Simple aliphatic aldehydes in aqueous solution behave quite differently on photo-oxidation by Ce^{IV} , yielding instead the alkyl radical R^\cdot from RCHO (or $\text{RCH}(\text{OH})_2$ as it exists in solution) in a manner similar to that of aliphatic alcohols (chapter 3). The production of R^\cdot is exclusive when $\text{R} = \text{H}$, or C_2H_5 and to an extent of $\sim 90\%$ when $\text{R} = \text{CH}_3$, the remaining 10% of absorption in the latter case coming from a 1:2:1 triplet ascribed to $\dot{\text{C}}\text{H}_2\text{CHO}$ or more probably its hydrated form $\dot{\text{C}}\text{H}_2\text{CH}(\text{OH})_2$. The differences in the product radicals are probably due to the quite extensive hydration of the carbonyl group under the conditions of method A to give, as the reactant, $\text{RCH}(\text{OH})_2$.

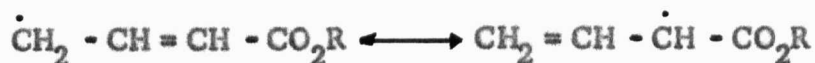
Ketones

With these substrates only differences of detail exist between the mechanism of photo-oxidation found in aqueous and non-aqueous solution. The simplest ketones, CH_3COCH_3 , $\text{CH}_3\text{COC}_2\text{H}_5$ and $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ all gave a mixture of two radicals corresponding to C-H and R-CO fissions, the former mode occurring at the most alkylated carbon atom. Exclusion of water from the reaction medium accentuated the degree of C-H fission, this becoming the exclusive pathway for ethyl and higher ketones. Methyl isopropyl, diisopropyl and dicyclopropyl were all examined under non-aqueous conditions and gave as the exclusive radical the αC -H fission product. This closely parallels the behaviour of OH both in the liquid and solid state where abstraction from the α -position occurs more readily than a similar process from the β -position.

Esters

Only the simplest members could be examined in aqueous solution using Ce^{IV} perchlorate, yielding under these conditions the methyl radical from both $\text{CH}_3\text{CO}_2\text{CH}_3$ and $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$, indicating C-C cleavage to give, presumably, the methyl or ethyl hydrogen carbonate as the other product. In neat ester or CH_3CN solution, a process of C-H bond fission is also operative, yielding $\dot{\text{C}}\text{H}_2\text{CO}_2\text{R}$ ($\text{R} = \text{CH}_3$ or C_2H_5). This mode dominates with non-aqueous solutions of higher homologues producing such radicals as $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{CH}_3$, $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCO}_2\text{C}_2\text{H}_5$ and $(\text{CH}_3)_2\dot{\text{C}}\text{CO}_2\text{CH}(\text{CH}_3)_2$ from the corresponding esters. Crotonate esters

are also oxidised by C - H fission, yielding allyl-type radicals,



but methyl cyanoacetate gave CH_2CN radical by C - C fission in a manner similar to the simplest esters studied in aqueous solution; this behaviour has also been observed with carboxylic acids as the main mode of decomposition (chapter 4).

As indicated in the results section (5.2.3.), methyl methacrylate undergoes C - H fission to yield monomeric $\dot{\text{C}}\text{H} = \text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ which, on warming from 77°K to 175°K, induces vinyl polymerisation to yield the well known nine-line spectrum of $\sim\text{CH}_2 - \dot{\text{C}}(\text{CH}_3)\text{CO}_2\text{CH}_3$, also observed with methyl vinyl radical produced from methacrylic acid (page 44) and which has been analysed by Symons¹⁶⁸ in terms of coupling from three equivalent protons and coupling from two slightly inequivalent protons as described in chapter 4 (page 51).

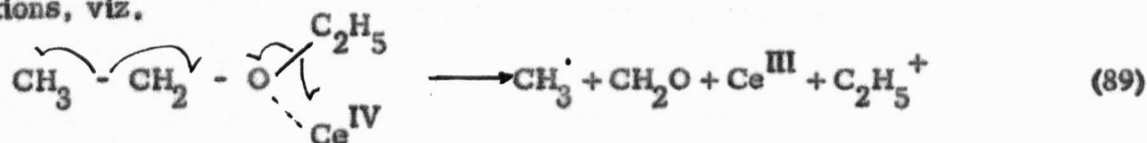
Amides

The mechanism of Ce^{IV} photo-oxidation of amides bears a strong resemblance to the radiolysis of the same compounds,¹⁸² where (i) N-alkyl and N,N-dialkyl-amides lose a proton on the carbon atom of the alkyl group adjacent to the nitrogen atom to give $\text{RCON}(\text{R})\dot{\text{C}}\text{HR}$ and (ii) non N-substituted amides react by loss of a proton on the carbon atom adjacent to the carbonyl group to give $\text{R}\dot{\text{C}}\text{HCONH}_2$. In the compounds studied in this work, dimethylformamide gives $\text{HCON}(\text{Me})\dot{\text{C}}\text{H}_2$ and acetamide gives $\dot{\text{C}}\text{H}_2\text{CONH}_2$. Acetamide gives also $\text{CH}_3\dot{\text{C}}$ during photo-oxidation by Ce^{IV} in acidic medium, and this is probably due to different species existing in acid solution, similar in manner to the reactions of ketones in an aqueous acidic medium (page 56) where, for example, acetone gives a mixture of $\text{CH}_3\dot{\text{C}}$ and $\dot{\text{C}}\text{H}_2\text{COCH}_3$. The obvious anomaly to this system is formamide which has no carbon atoms adjacent to either the carbonyl group or the nitrogen atom; oxidation by removal of an H-atom could lead to formation of either $\dot{\text{C}}\text{ONH}_2$ or $\text{HCON}\dot{\text{H}}$. $\dot{\text{C}}\text{ONH}_2$ radical is formed during u.v. photolysis of formamide¹⁸⁴ and radicals of the type $\text{RCONH}\dot{\text{C}}$ are formed during γ -irradiation of urea¹⁸⁶ at 77°K. It is fairly certain that the radical observed in this work is $\dot{\text{C}}\text{ONH}_2$ for two reasons, (i) the radical produced on photo-oxidation of formamide by Ce^{IV} exhibited no observable anisotropic effects and (ii) showed isotropic couplings of 30.0 (for ^1H) and 22.0 Oe (for ^{14}N) throughout the temperature range 77° - 175°K. Similar couplings have been reported for this

species both in solid¹⁸² and liquid phase studies.¹⁸⁰ The other radical, $\text{R}\dot{\text{C}}\text{ONH}$, is known to exhibit strong isotropic effects at 77°K, although the magnitude of the couplings are similar to those found for $\dot{\text{C}}\text{ONH}_2$. The most striking difference is in the ^{13}C couplings which we were unable to observe; Symons,¹⁸⁶ however, had made a study of ^{13}C coupling in $\dot{\text{C}}\text{ONH}_2$ and finds it in the same order of magnitude as that found in acyl-type radicals. Consequently, $\dot{\text{C}}\text{ONH}_2$ is believed to be a σ -radical. It is significant that even in solution this radical exhibits hyperfine coupling to two inequivalent protons. This shows that rotation about the C-N bond is highly restricted, which suggests that the atoms of the NH_2 group are coplanar with the C=O group and that π -bonding between carbon and nitrogen is perhaps important.

Ethers

The results obtained from photo-oxidation of ethers are limited in number; however, it seems that the main mechanism is one of C-H cleavage to give RCHOR and this reaction is observed with diethyl ether, tetrahydrofuran and probably 1,3- and 1,4-dioxan. The observation of $\text{CH}_3\dot{\text{C}}$ during photo-oxidation of diethyl ether by Ce^{IV} in acidic solution is consistent with a mechanism analogous to that proposed for the production of $\text{CH}_3\dot{\text{C}}$ during photo-oxidation of ethanol (page 31), isopropanol (page 32) and t-butanol (page 33) under the same conditions, viz.



The behaviour of Ce^{IV} closely parallels that of OH^{\cdot} ¹¹¹ in the reactions with ethers to give α -H abstraction products; similar intermediates are observed during γ -radiolysis of ethers.¹⁰³ Photo-sensitised decomposition by naphthalene,¹⁸⁷ however, yields $\text{C}_2\text{H}_5\dot{\text{C}}$. The mechanism involves direct energy transfer from an excited naphthalene molecule to the solvent with subsequent dissociation of the highly excited solvent molecule and in the case of naphthalene, the energy arises from an initial triplet-triplet absorption of light. Although $\text{C}_2\text{H}_5\dot{\text{C}}$ is observed in these experiments, the primary species formed is $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$ which decomposes on prolonged photolysis to $\text{C}_2\text{H}_5\dot{\text{C}}$ and CH_3CHO . Presumably the observation of $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$ in this work is due to the short irradiation time and high quantum yield of the Ce^{IV} -diethyl ether system.

CHAPTER 6

U^{VI} PHOTO-OXIDATION OF ORGANIC COMPOUNDS

6. U^{VI} PHOTO-OXIDATION OF ORGANIC COMPOUNDS

6.1 Introduction

The photochemistry of the uranyl ion, UO_2^{2+} , in solution is complicated but well-documented as mentioned earlier (page 3). It is known to form complexes with a variety of organic and inorganic compounds. Photochemical studies up to 1962 have been reviewed comprehensively by Rabinowitch and Belford,⁵ who point out that the photochemistry of U^{VI} was one of the most extensively studied, yet also the least understood areas in photochemistry. Their call to examine U^{VI} photochemistry precisely and with modern techniques to obtain a clearer understanding of the primary processes involved, has gone largely unheeded.

In the preceding three chapters, the cryogenic photolysis technique has been applied extensively to the study of the photochemistry of complexes of the Ce^{IV} ion with organic substrates with considerable success. It is the purpose of this chapter to use the same technique to study the analogous reactions of U^{VI} . Three main groups of compounds have been studied, namely, alcohols, acids and ketones, together with a number of exploratory examinations of other systems and certain parts of this work obviously require further development. I would like to thank Mr. R. J. Hill who performed some of the experiments with carboxylic acids and whose results I quote herein to amplify discussion of my own work. The experiments performed by Mr. R. J. Hill are marked thus*.

Sample preparations were largely as before; U^{VI} concentrations of up to 0.3 M were used and, because of the high solubility and slow thermal reactions between UO_2^{2+} ions and organic substrates, most compounds were examined by method C. Uranyl perchlorate and nitrate were both used, but most work was done with the perchlorate salt to avoid confusion of some of the wing peaks of the organic radicals formed with NO_2^{\cdot} , produced when the nitrate salt was used, i.e. in a similar manner to NO_2^{\cdot} production from ceric ammonium nitrate (page 30). Because of its mildly thermal oxidising properties, the photo-oxidations of hydroxy acids, thio acids and α, β -unsaturated ketones could be studied. (The analogous reactions with Ce^{IV} proceed too quickly to allow adequate sample preparation).

Since the absorption of UO_2^{2+} tends to be large only at wavelengths $\lambda < 300 \text{ nm}$, all the experiments, unless otherwise indicated, were performed with unfiltered light. This can lead to direct photolysis of the organic substrate and production of a radical not derived from photo-oxidation by the metal ion. By suitable 'blank' experiments and use of short irradiation times, the effect of direct photo-decomposition was found to be minimal, and for most cases, non-existent.

6.2 Results

6.2.1. Alcohols

Methanol - Photolysis by method C yielded a distorted but recognisable triplet with $a_{\text{H}} = 19.0 \pm 2.0 \text{ Oe}$, similar to that obtained during Ce^{IV} photo-oxidation and other low temperature oxidations of methanol, which is assigned to CH_2OH radical.

Ethanol - Examination at 77°K produced a five-line binomial spectrum with $a_{\text{H}} = 21.0 \text{ Oe}$, assigned to CH_3CHOH radical on comparison with the spectra produced from photolysis of solutions of ethanol and H_2O_2 at 77°K .¹³¹

Propan-2-ol - Method C gave CH_3^\bullet radical only (figure 24 (a)) with $a_{\text{H}} = 23.4 \text{ Oe}$ and clearly, C - C bond cleavage is taking place in this instance.

Butan-2-ol - Photolysis of a solution of uranyl perchlorate in neat butan-2-ol at 77°K yielded a spectrum attributed to $\text{C}_2\text{H}_5^\bullet$ radical ($a_{\text{CH}_3}^{\text{H}} = 26.7 \text{ Oe}$, $a_{\text{CH}_2}^{\text{H}} = 21.0 \text{ Oe}$) and once again, C - C bond cleavage has taken place to the exclusion of any α - H abstraction process. Similar experiments with ceric ammonium nitrate produced a mixture of radicals including CH_3^\bullet and a smaller triplet species. The spectrum obtained at 77°K is shown in figure 24 (b).

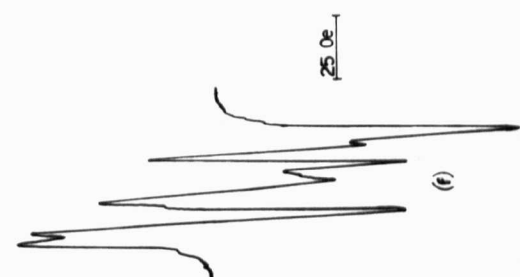
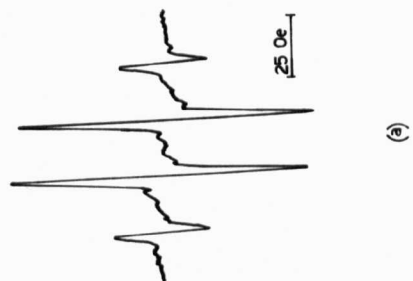
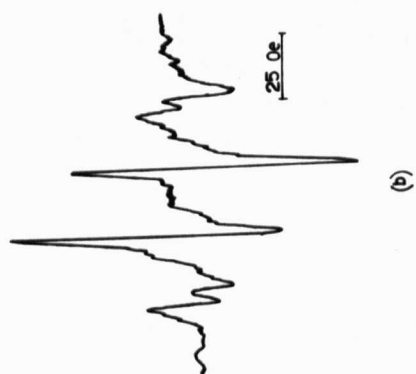
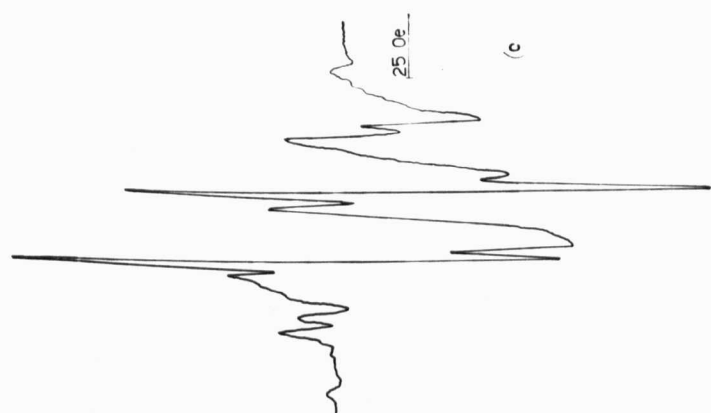
Pentan-3-ol - Initial photolysis at 77°K produced a broad 1 : 3 : 3 : 1 spectrum ($a_{\text{H}} = 26.6 \text{ Oe}$) assigned to $\text{C}_2\text{H}_5^\bullet$, the lines being sufficiently broad to render resolution of the smaller methylene proton splittings difficult. Warming to 175°K caused the radical to decay completely and rephotolysis at this temperature produced a six-line spectrum of approximately binomial intensity with $a_{\text{H}} = 22.5 \text{ Oe}$ which disappeared at 200°K . Photolysis of a fresh sample at 175°K resulted in formation of a well-resolved $\text{C}_2\text{H}_5^\bullet$ spectrum shown in figure 24 (c) ($a_{\text{CH}_3}^{\text{H}} = 26.7$, $a_{\text{CH}_2}^{\text{H}} = 21.3 \text{ Oe}$). Warming to 200°K gave a smaller, broad spectrum which decayed quickly at this temperature.

Tert-butanol - Examination by method C yielded a spectrum of intensity

FIGURE 24

**E.S.R. Spectra Obtained During Photo-Oxidation of
Alcohols by U^{VI}**

- (a) Propan-2-ol at 77°K**
- (b) Butan-2-ol at 77°K**
- (c) Pentan-3-ol at 175°K**
- (d) tert-Butanol at 245°K**
- (e) 3-Methylhexan-3-ol rephotolysed at 175°K**
- (f) Propargyl alcohol at 77°K**



distribution 1:3:3:1 with $a_H = 23.4$ Oe and is accordingly assigned to CH_3^\bullet . Warming the sample to 120°K effected a reduction in CH_3^\bullet absorption and the appearance of a new three-line spectrum ($a_H = 21.7$ Oe); further warming to 160°K resulted in complete loss of CH_3^\bullet leaving only the three-line spectrum of intensity distribution 1:2:1, which decayed slowly at this temperature. Photolysis of a fresh sample at 245°K produced the spectrum shown in figure 24 (d). Clearly, at this temperature, the only observable absorption is the three-line one, characteristic of CH_2^\bullet -R radicals of which $\text{CH}_2^\bullet\text{C}(\text{Me})_2\text{OH}$ is the most likely species.

1,1-Dimethylpropan-1-ol - Photolysis of a solution of uranyl nitrate in neat alcohol at 77°K produced a spectrum of $\text{C}_2\text{H}_5^\bullet$ identified by the splitting of 26.4 Oe between the two largest peaks. Warming to 160°K resulted in the disappearance of $\text{C}_2\text{H}_5^\bullet$.

2,3-Dimethylbutan-2-ol - Method C gave a weak six-line spectrum of approximate binomial intensity ($a_H = 22.1$ Oe) which is tentatively assigned to $(\text{CH}_3)_2\text{CH}^\bullet$ radical, assuming that the spectral intensity was insufficient to enable resolution of the two outermost wing peaks. Solid state studies of $(\text{CH}_3)_2\text{CH}^\bullet$ have produced an eight-line spectrum with $a_H = 26.4 \pm 0.8$ Oe¹⁰⁴ and the liquid phase spectrum shows splittings of $a_{\text{CH}_3}^H = 24.6$, $a_{\text{CH}}^H = 22.2$ Oe.¹⁰⁵

3-Methylhexan-3-ol - Photolysis at 77°K produced $\text{C}_2\text{H}_5^\bullet$ with $a_{\text{CH}_3}^H = 26.0$, $a_{\text{CH}_2}^H = 20.9$ Oe. Warming in the dark to 175°K resulted in the complete decay of $\text{C}_2\text{H}_5^\bullet$. Rephotolysis at this temperature gave a complex spectrum consisting of five main lines shown in figure 24 (e). Photolysis of a fresh sample at 175°K yielded only $\text{C}_2\text{H}_5^\bullet$ indicating that the five-line species is a product of secondary reactions. Similar experiments with Ce^{IV} gave a spectrum consisting of a mixture of radicals, the analysis of which proved very difficult, but $\text{C}_2\text{H}_5^\bullet$ was one contributing species.

Benzyl alcohol - Investigation by method C produced a strong signal of the now familiar benzyl radical ($a_{\text{CH}_2}^H = 16.6$ Oe, $a_{2,4,6}^H = 5.6$ Oe). This, however, is a highly anomalous result inasmuch as production of benzyl radical from benzyl alcohol is a reductive process, implying oxidation of U^{VI} . Warming to 140°K produced an increase in resolution and the signal finally decayed at 175°K . Benzyl alcohol was apparently inert to photo-oxidation by ceric ammonium nitrate (page 35).

2-Phenylethanol - Examination at 77°K gave the spectrum of $C_6H_5CH_2^{\cdot}$, i.e. behaviour identical to that observed during Ce^{IV} photo-oxidation with splitting constants $a_{CH_2}^H = 16.5$, $a_{2,4,6}^H = 5.4$ Oe. Warming to 175°K resulted in complete decay of the radical. Rephotolysis at this temperature produced only the benzyl radical.

Propargyl alcohol - Method C yielded a six-line spectrum shown in fig. 24 (f) and analysed in terms of splitting from two approximately equivalent protons ($a_{OH}^H = 4.8$ Oe) and a smaller splitting ($a_{CH}^H = 12.0$ Oe) from one proton, and assigned to $CH \equiv C - CHOH$ radical. Similar spectra have been produced from photo-oxidation of propargyl alcohol by H_2O_2 at 77°K.¹³⁶ Warming to 175°K effected no change and the radical decayed at this temperature.

Ethylene glycol - Photolysis by method C gave only a poor, three-line spectrum with $a_H = 19.0$ Oe, similar to that obtained by Ce^{IV} photo-oxidation of the same alcohol and assigned to $HO\dot{C}HCH_2OH$ radical.

6.2.2. Acids

Formic acid* - Photolysis of a solution of uranyl perchlorate in neat formic acid at 77°K produced only a singlet exhibiting anisotropy of the g-tensor and analysed as $g_1 = 2.0047$, $g_2 = 2.0015$, $g_3 = 1.9951$, similar to spectrum C observed on warming a photolysed solution of Ce^{IV} and formic acid to 115°K (page 41) which has been assigned to $\dot{C}O_2H$ radical. The absence of H-atoms and the immediate production of $\dot{C}O_2H$ leads to the conclusion that C-H bond breaking, and not decarboxylation followed by subsequent thermal reaction, is the primary photo-chemical process, in accord with the mechanism proposed by Oullet based on product studies and quantum yield measurements.¹⁸⁸

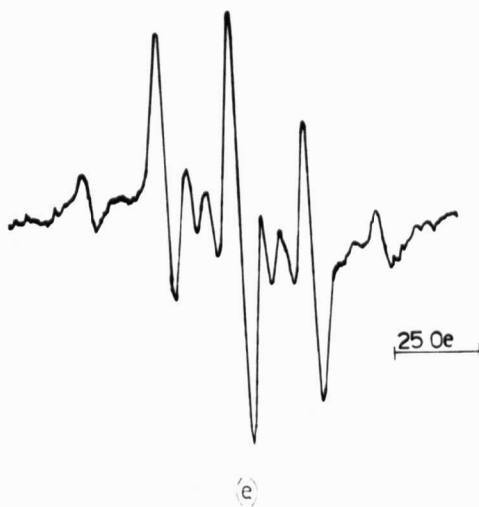
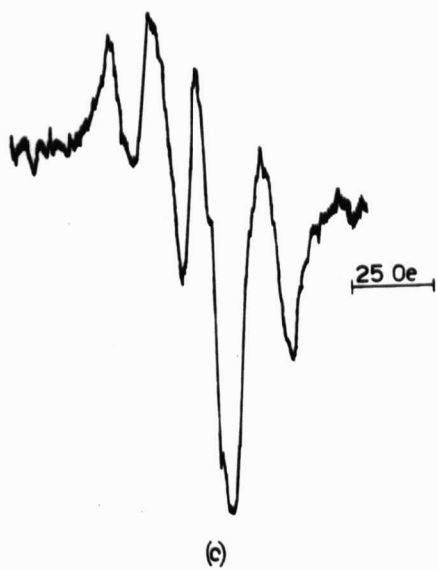
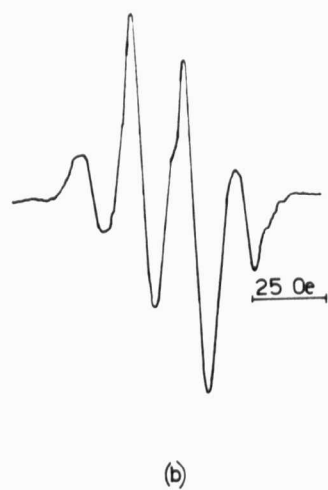
Acetic acid - Method C yielded, at 77°K, a mixture of two radicals, a sharp four-line spectrum of binomial intensity with $a_H = 22.8$ Oe attributed to CH_3^{\cdot} , and a smaller distorted triplet with $a_H = 21$ Oe assigned to $\dot{C}H_2CO_2H$ by comparison with other solid state spectra reported¹⁶¹ for $\dot{C}H_2CO_2H$. Warming to 140°K effected a decrease in the intensity of CH_3^{\cdot} radical until only the triplet remained, which itself decayed slowly at 160°K.

Propionic acid - Examination by methods A and C gave identical results, namely a five-line spectrum of binomial intensity with $a_H = 24.4$ Oe. Warming to 140°K in the dark effected no change and further warming in the dark to 175°K caused the radical to decay completely. The spectrum is analysed in terms of

FIGURE 25

**E.S.R. Spectra Obtained During Photo-Oxidation of
Carboxylic Acids by U^{VI}**

- (a) Isobutyric Acid at $77^{\circ}K$**
- (b) Lactic Acid at $77^{\circ}K$**
- (c) Thiolactic Acid at $77^{\circ}K$**
- (d) Thioglycollic Acid at $77^{\circ}K$**
- (e) Methacrylic Acid at $200^{\circ}K$**



four approximately equivalent protons, the most probable radical being $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{H}$ by comparison with other acids studied in this chapter, and also with the spectrum of $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{H}$ produced from γ -irradiated alanine¹⁸⁹ with $a_{\text{H}} = 25.0$ Oe. The corresponding reactions with Ce^{IV} and OH^\bullet yield $\text{C}_2\text{H}_5^\bullet$ (page 41) and $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CO}_2\text{H}$ respectively.¹¹¹

Isobutyric acid - Method A yielded a seven-line spectrum shown in fig. 25 (a) with $a_{\text{H}} = 20.5$ Oe. The radical is presumably $(\text{CH}_3)_2\dot{\text{C}}\text{CO}_2\text{H}$ formed by abstraction of the hydrogen atom adjacent to the carboxyl group. Warming to 175°K in the dark caused only a decrease in signal intensity due to thermal decay.

Trifluoroacetic acid* - Examination by method C at 77°K produced a broad spectrum extending over ca. 400 Oe, exhibiting considerable anisotropy. Warming to 160°K effected little change, and it was analysed in terms of $g_1 = 2.0006$, $a_1 = 215$ Oe, $g_2 = 2.0053$, $a_2 = 122$ Oe, $g_3 = 2.0080$, $a_3 = 76$ Oe ($g_{\text{iso}} = 2.0046$) and assigned to CF_3^\bullet , agreeing reasonably well with other reports of CF_3^\bullet in solid matrices.¹⁶⁰

Lactic acid - An acid solution of lactic acid and uranyl perchlorate ($\text{pH} = 1$) gave, on photolysis at 77°K , a broad 1:3:3:1 spectrum shown in figure 25 (b), with $a_{\text{H}} = 17.4$ Oe and attributed to $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{H}$. Solution studies of this radical formed by oxidation of lactic acid with $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ couple in a rapid flow system¹¹¹ gave $a_{\text{CH}_3}^{\text{H}} = 17.1$, $a_{\text{OH}}^{\text{H}} = 2.0$ Oe; clearly, line broadening effects in the solid state would not allow us to resolve the small hydroxyl proton splitting. A report on the photo-oxidation of lactic acid by uranyl ions shows different pathways at differing pH and the cryogenic photolysis experiment was repeated at pH 7 producing a mixture of radicals, consisting of a five-line spectrum ($a_{\text{H}} = 21.8$ Oe) and a four-line spectrum ($a_{\text{H}} = 17.0$ Oe). Warming in the dark to 175°K resulted in the disappearance of the five-line species, leaving only the four-line spectrum identical to that produced from an acidic solution of U^{VI} and lactic acid. The five-line species is attributed to $\text{CH}_3\dot{\text{C}}\text{HOH}$ formed by decarboxylation, and the four-line one to $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{H}$. γ -radiolysis of lactic¹⁹⁰ acid yields a five-line spectrum with $a_{\text{H}} = 22 \pm 2$ Oe, presumably due also to $\text{CH}_3\dot{\text{C}}\text{HOH}$.

α -Hydroxyisobutyric acid* - Photolysis of a solution of carefully purified acid and uranyl perchlorate produced no appreciable absorption at 77°K or even when the temperature was raised to 175°K with the full light source on.

Thiolactic acid - Method C yielded a distorted four-line spectrum shown in figure 25 (c) with $a_H = 18 \pm 2$ Oe, which is assigned to $\text{CH}_3\dot{\text{C}}(\text{SH})\text{CO}_2\text{H}$ radical.

Thioglycolic acid - Examination at 77°K gave a doublet spectrum shown in figure 25 (d) with $a_H = 18.0$ Oe and attributed to $\dot{\text{C}}\text{H}(\text{SH})\text{CO}_2\text{H}$. The corresponding hydroxy radical, $\text{CH}(\text{OH})\text{CO}_2\text{H}$, has been observed in solution with $a_{\text{CH}}^{\text{H}} = 15.0$ Oe and $a_{\text{OH}}^{\text{H}} = 3$ Oe.

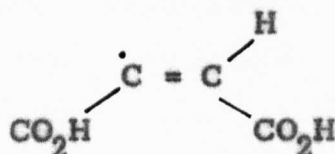
Cyclopropanecarboxylic acid - Examination by method C yielded a complex asymmetric spectrum, not assignable to the cyclopropyl radical which is observed in similar experiments with Ce^{IV} .

Oxalic acid* - Photolysis at 77°K of a solution of oxalic acid and uranyl perchlorate gave a poorly resolved singlet with $g_{\text{av}} = 2.014$. It seems unlikely that this radical is CO_2H because the established value of g_{av} for the latter is 2.0006.¹⁶⁵

Malonic acid* - Method A gave a distorted spectrum very similar to that obtained with Ce^{IV} photo-oxidation of malonic acid and assigned to $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$ with $a_H = 21 \pm 1$ Oe. Warming the sample to 140°K caused a reduction in intensity and the spectrum finally decayed completely at 175°K . Renewed photolysis at this temperature produced only the triplet spectrum.

Fumaric*, Succinic acids* - Poor spectra were obtained which did not permit a worthwhile analysis.

Maleic acid* - Photolysis at 77°K yielded no observable radical species; however, warming to 140°K and rephotolysis gave a doublet spectrum with $a_H = 22.4$ Oe, typical of the interaction between one proton and the free electron. Accordingly, the radical species is presumed to be



which is in effect, a substituted vinyl radical, a species characterised by large β coupling constants.

1,1-Cyclobutanedicarboxylic acid - Examinations by methods A and C failed to produce any observable spectra.

Methacrylic acid* - Initial photolysis at 77°K gave a weak absorption with insufficient resolution to enable reasonable analysis. Warming to 175°K and re-photolysing produced a larger spectrum which consisted of five main lines

($a_H = 22.5$ Oe) with four shoulders. Continued warming to 200°K enabled the shoulders to be resolved into two lines, shown in figure 25(e). The spectra are consistent with an assignment to the polymethacrylic acid radical which is analysed in terms of splitting from three equivalent protons of 22.5 Oe and two non-equivalent protons of 14.7 and 8.3 Oe respectively. This agrees well with the assignment of Bamford et al.¹⁶⁹ who observed the radical during u.v. irradiation of methacrylic acid at 240°K and analysed it in terms of $a_{\text{CH}_3}^H = 23.2$, $a_{\text{CH}(1)}^H = 15.15$, $a_{\text{CH}(2)}^H = 8.05$ Oe.

Acrylic acid* - Photolysis at 77°K by method C yielded no spectrum but warming and rephotolysing at 160°K yielded a five-line spectrum already tentatively assigned to the polyacrylic acid radical (page 43).

6.2.3. Ketones

Acetone* - Method A yielded at 77°K a four-line spectrum assigned to CH_3^\bullet ($a_H = 22.4$ Oe) in good yield, and a minor component, but warming in the dark to 160°K caused a decrease in CH_3^\bullet absorption and a new three-line absorption became apparent with $a_H = 21.0$ Oe. Photolysis of a solution of uranyl perchlorate in neat acetone produced CH_3^\bullet and the three-line species in approximately equal concentrations. Warming to 165°K in the dark resulted in the disappearance of CH_3^\bullet leaving only the triplet species. The three-line spectrum comes from a radical of the type $\text{X}-\text{CH}_2^\bullet$ of which $\dot{\text{C}}\text{H}_2\text{COCH}_3$ is the most likely, arising from CH_3^\bullet attack on CH_3COCH_3 or from α -H abstraction from acetone by an excited uranyl ion.

Methylethyl Ketone - Examination by method C yielded a mixture of radicals, namely, $\text{C}_2\text{H}_5^\bullet$ identified by the splitting of 26.8 Oe between its two largest peaks and a smaller five-line spectrum of approximately binomial intensity distribution with $a_H = 20.6$ Oe. Warming to 140°K in the dark left only the five-line species which is attributed to $\text{CH}_3\dot{\text{C}}\text{HCOCH}_3$ on the basis of comparison with other solid state spectra of this species.

Pentan-3-one* - Photolysis of a frozen solution of uranyl perchlorate in neat solvent at 77°K gave a five-line binomial spectrum similar to that obtained with methylethyl ketone and uranyl ion, and exhibiting a hyperfine coupling of $a_H = 21.9$ Oe. This is assigned to the $\text{CH}_3\dot{\text{C}}\text{HCOCH}_2\text{CH}_3$ radical. Warming the sample to 175°K resulted in complete disappearance of the radical.

FIGURE 26

**E.S.R. Spectra Obtained During Photo-Oxidation of
Ketones by U^{VI} at $77^{\circ}K$**

- (a) Methylisopropyl Ketone**
- (b) 3-Penten-2-one**



2,2,4,4-Tetradeuteropentan-3-one* - Examination by method C at 77°K gave a broad, four-line spectrum with $a_H = 21.5$ Oe. This spectrum is attributed to $\text{CH}_3\dot{\text{C}}\text{DCOCD}_2\text{CH}_3$ radical where the splittings due to the D-atoms are not observed due to the line-broadening process in the solid state.

Methylisopropyl Ketone* - Method C yielded a seven-line binomial spectrum shown in figure 26(a) with $a_H = 19.9$ Oe which decayed when warmed in the dark to 175°K. The seven-line species is assigned to $(\text{CH}_3)_2\dot{\text{C}}\text{COCH}_3$, which has been observed during experiments involving Ce^{IV} and methylisopropyl ketone (page 56).

3-Penten-2-one* - A four-line spectrum typical of allylic-type radicals was observed with $a_H = 13.0$ Oe showing some slight resolution on the first and last peaks (fig. 26(b)). Warming to 150°K had no great effect on the resolution and finally the radical decayed completely in the dark at 190°K. From the nature of the hyperfine pattern and the magnitude of the coupling constant, the radical produced is probably $\dot{\text{C}}\text{H}_2\text{-CH=CH-COCH}_3$. The radical $\text{CH}_3\text{CH}=\dot{\text{C}}\text{-COCH}_3$ produced by α -hydrogen atom abstraction would be expected to show much larger coupling constants being a substituted vinyl radical.

6.2.4. Other Organic Compounds

Acetonitrile - Photolysis by method C at 77°K yielded a large signal identical to that observed by Volman et al. from photolysis of solid acetonitrile with irradiation of $\lambda = 185$ nm and assigned to $\text{CH}_2\dot{\text{C}}\text{N}$. It is interesting to note that these authors found $\text{CH}_3\dot{\text{C}}\text{N}$ inert to all radiation of $\lambda > 200$ nm, so strengthening the case for electron transfer to UO_2^{2+} ions observed in this work. Warming to 160°K caused the radical to decay completely.

Ethylcrotonate - Examination by method C produced a four-line spectrum with $a_H = 13.4$ Oe and assigned to $\text{CH}_3\text{-CH}=\dot{\text{C}}\text{H-CO}_2\text{C}_2\text{H}_5$ radical which has been observed from Ce^{IV} photo-oxidation of the same substrate (page 59).

Propionaldehyde - Photolysis of a solution of uranyl perchlorate in neat propionaldehyde at 77°K yielded a spectrum assigned to $\text{C}_2\text{H}_5\dot{\text{C}}\text{H}$ with $a_{\text{CH}_2}^{\text{H}} = 20.2$ Oe, $a_{\text{CH}_3}^{\text{H}} = 26.9$ Oe and a second, smaller absorption consisting of a number of lines spaced between the absorption lines of $\text{C}_2\text{H}_5\dot{\text{C}}\text{H}$. Leaving the sample in the dark for thirty minutes resulted in some loss of $\text{C}_2\text{H}_5\dot{\text{C}}\text{H}$ with a corresponding increase in the second species which now appeared to be approximately binomial in intensity distribution and consisting of five lines with $a_H = 21.3$ Oe. The spectrum is ascribed to $\text{CH}_3\dot{\text{C}}\text{HCHO}$ radical formed when $\text{C}_2\text{H}_5\dot{\text{C}}\text{H}$ reacts thermally with propionaldehyde by an α -H abstraction process.

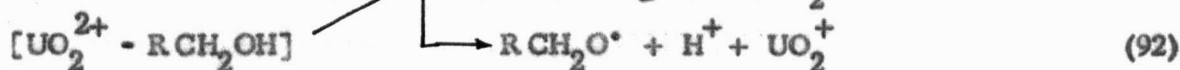
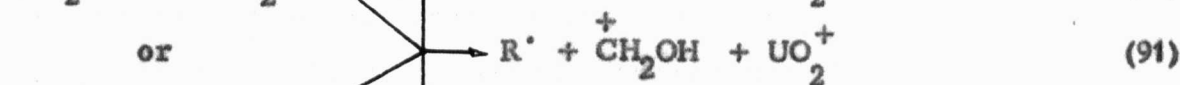
DISCUSSION

Alcohols

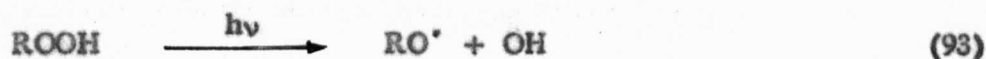
A number of possible mechanisms for the photo-oxidation of alcohols by uranyl ion are possible, viz.



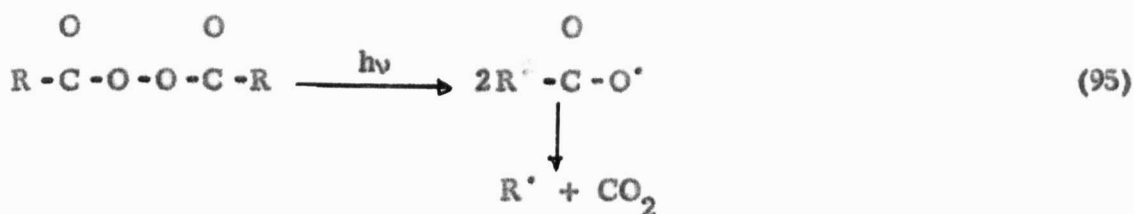
or



followed by (i) oxidation of the radical formed to R^+ and (ii) disproportionation of UO_2^+ to UO_2^{2+} and UO_2 . Most reports based on product studies and radical scavenging experiments invoke reaction (90) for primary and secondary alcohols and reaction (91) for tertiary alcohols. In agreement, methanol produces CH_2OH and ethanol CH_3CHOH in the experiments from this work. However, a recent report using spin-trapping methods, on the photo-oxidation of methanol by uranyl nitrate proposes production of $\text{CH}_3\text{O}^\cdot$ as the primary process,¹⁹¹ with CH_2OH resulting from isomerisation or abstraction reactions of $\text{CH}_3\text{O}^\cdot$. This is, however, a preliminary communication and a detailed study on a large number of alcohol molecules has not yet been reported. The absence of any e.s.r. absorption due to RO^\cdot observed in our work does not, however, discount its existence. Alkoxy radicals (RO^\cdot) are believed to be the precursors of peroxy radicals (RO_2^\cdot) formed by photolysis of hydroperoxide glasses at cryogenic temperatures and observed by e.s.r., viz.



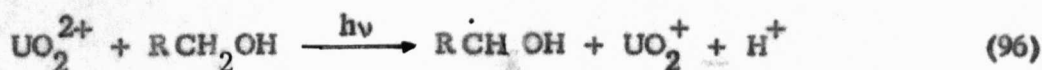
With reaction (94) occurring very rapidly even at 77°K , abstraction from a C-H group of another molecule by an alkoxy radical could explain the production of RCHOH from primary alcohols observed during photo-oxidation by U^{VI} . However, production of alkyl radicals from substituted alcohols is difficult to explain by this mechanism for it implies rearrangement of the alkoxy radical to give a ketone and an alkyl fragment, and such a process has only been observed with a number of diacyl peroxides,¹⁹² viz.



where the elimination of a small, simple molecule like CO_2 renders the photolysis irreversible, and it seems unlikely, therefore, that such a process pertains for the photo-oxidation of substituted alcohols by U^{VI} .

The main primary reaction mechanisms proposed for U^{VI} photo-oxidation are (i) the kinetic encounter mechanism (page 4) and (ii) the complex formation mechanism (page 5) and both could apply equally well in the cases discussed here. It is very difficult to distinguish between these mechanisms by e.s.r. alone, for both photo-induced electron- and energy-transfer processes occur with great efficiency at 77°K , as evident from the work with Ce^{IV} , so this problem of differentiating between the primary physical processes remains, to this extent, unresolved.

It is clear from the e.s.r. spectra observed in this work that the primary photochemical process involved in UO_2^{2+} photo-oxidation of primary and allylic alcohols is one of abstraction of an α -H atom, in keeping with similar reactions of Ce^{IV} (page 30) and OH^{\cdot} ,¹¹⁰ viz.

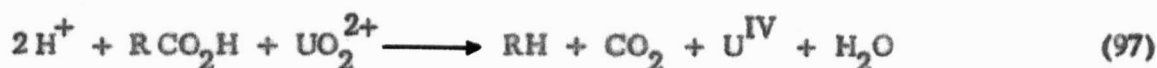


Secondary and tertiary alcohols yield as the main component, an alkyl radical derived from C-C bond fission, production of the most stable alkyl radical being the commonest pathway. Thus, 2-methylbutan-2-ol gives $\text{C}_2\text{H}_5^{\cdot}$ and 2,3-dimethylbutan-2-ol yields $(\text{CH}_3)_2\dot{\text{C}}\text{H}$ as the main radical species. This type of mechanism is well in accord with the known thermal oxidations of substituted alcohols by metal ions.¹⁴⁶ The reaction of benzyl alcohol and U^{VI} is hard to explain and warrants further work.

Acids

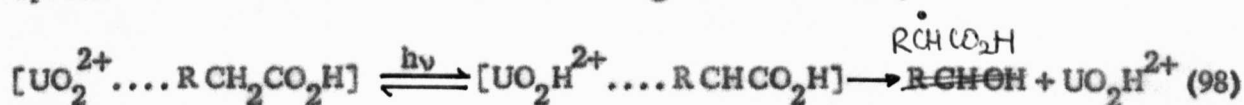
The photosensitivity of simple carboxylic acids towards uranyl ions has long been established (page 5), the main products of the reaction being CO_2 and a hydrocarbon and the following two principal mechanisms have been proposed for the primary process :

- (i) photosensitised decomposition, whereby the reaction proceeds with no appreciable loss of U^{VI} , presumably through oxidation of one part of the organic substrate by excited uranyl ions, whose reduction products, U^V and U^{IV} , are then, according to Heidt,³⁷ re-oxidised back to uranyl ions by the other part of the organic molecule,
- (ii) direct photo-oxidation, whereby the reaction proceeds to give decomposition products of the acids and also reduced uranium species, viz.



It is proposed to show that both of these mechanisms are, in fact, identical as regards their primary processes and that the reactivity of the primary products determines the subsequent mechanism. From the e.s.r. spectra obtained, it would appear that the primary process is abstraction of an α -H atom to give $RCHCO_2H$, and this species is observed with all acids apart from malonic acid.

Decarboxylation to yield R^\cdot is normally only of minor importance, being observed with acetic acid (along with production of $\dot{C}H_2CO_2H$), but is the exclusive route with malonic and trifluoroacetic acids. This is in complete disparity with Ce^{IV} photo-oxidation of carboxylic acids, where the universal and exclusive process is that of decarboxylation to give R^\cdot . Certain acids failed to give any spectra at 77°K and this is attributable to cage recombination,



Warming the sample helps the caged pair to break apart and in the case of maleic acid, spectra are observed at 140°K. Succinic acid, known to form a 2:1 complex with uranyl ions,²⁸ presumably behaves in this manner; at temperatures high enough for the caged pair to break down, the radicals probably react thermally and hence are not observed even on warming and photolysing the sample.

Product studies of UO_2^{2+} photo-oxidation of acids demonstrate carbon dioxide and a hydrocarbon are formed, and it is difficult to imagine how the radicals observed by e.s.r. in this work can react to give the required products. The answer to this problem lies in the nature of the intermediates formed from the initial photo-

with aerated samples of UO_2^{2+} and organic substrates indicated a photosensitisation mechanism, but this can be attributed to the rapid oxidation of U^{IV} by molecular oxygen.¹⁹⁴

The e.s.r. spectra produced have all been observed before and need little explanation; however, the apparent production of polymer radicals even at 77°K from acrylic and methacrylic acids suggests a radical reaction within the uranyl-acid complex. UO_2^{2+} is known to form specific complexes with organic acids of stoichiometry 1:1, 1:2 or higher, depending on the nature and concentration of the acid, and production of a monomer-type radical at 77°K within these complexes could result in rapid polymerisation by electron-transfer to another complexed acid molecule to yield the polymer radical.

CHAPTER 7

METAL-ION PHOTO-OXIDATIONS IN SOLUTION

7. METAL-ION PHOTO-OXIDATIONS IN SOLUTION

7.1 Introduction

From the previous four chapters, it is clear that photo-induced electron-transfer reactions between metal ions and organic substrates do indeed occur and that the reactive species formed can be trapped and stabilised by the matrix isolation method, allowing examination at leisure. While this technique is ideal for the study of primary processes, any extrapolation to explain features of the corresponding reactions in the liquid phase under steady-state irradiation are dubious. The dangers are similar to those inherent in any method that allows an artificially high concentration of reactive species to be formed, such as flash photolysis or pulse radiolysis. Such experimental approaches allow radical-radical recombination and reactions of excited states such as triplet-triplet annihilation to assume a far greater importance than under steady-state, low intensity, photolysis or radiolysis conditions. Accordingly, the logical extension of the work so far pursued is the study of metal ion electron-transfer reactions in the liquid phase under continuous steady-state irradiation with a view to observing the free radicals formed. This necessitates the development of a suitable flow system to enable replenishment of the sample and a short description follows.

7.1.1. Development of a Suitable Flow System

Bearing in mind the results of earlier experiments of metal ions in the solid state (chapters 3, 4, 5, 6), a simple flow cell was thought to be sufficient and a cell was constructed to fit the standard variable temperature accessory of Decca Radar Limited, supplied with the e.s.r. spectrometer. The outer body of the cell consisted of a piece of 4 mm. o/d 'Spectrosil' tubing fused via a graded seal to a Pyrex B 10 socket with a small take-off tube fitted just below the socket. The inner section of the cell was formed from a small 50 ml separating funnel and a B 10 cone fitted with a thick capillary reaching just to the bottom of the outer body when both halves were fitted. Filling the funnel with degassed solution under a nitrogen atmosphere and the application of a vacuum by a small electric pump to the take-off point effected a slow, downward flow of solution through the cell. This simple arrangement suffered from a large number of drawbacks, apart

from the fact that no radicals were observed when it was employed. For example, at low temperatures the viscosity of the solutions (usually alcohols) became too great for the small suction pump to maintain a flow of fluid. Again, although the Spectrosil tube has a large transmission factor ($> 95\%$ for $\lambda > 200 \text{ nm}$) the cylindrical surface of the tube scattered a large proportion of light, reducing the amount of light absorbed and consequently proving extremely inefficient.

The problem of maintaining a steady flow rate at all temperatures was tackled by employing a pumping system to force the viscous liquid through the cell. Initial experiments with a peristaltic pump (which failed to produce the required flow rates) showed that a very strong motor driven syringe unit would be required and accordingly such a system was constructed. It was found that a 2 r.p.m. motor (Parvalux, 35 lb/inches) coupled to a four-speed planet-type gearbox (constructed by Mr. C. Worland of the Departmental Workshop) worked admirably under all conditions, providing a regular and steady rate of flow.

Having designed and produced a slow flow system, the next stage of development was concerned with the modification of the cell system (a) to obtain the maximum amount of light absorbed and (b) to produce the maximum possible concentration of radicals. This necessitated the use of a thick, flat cell, the prototype of which was constructed from a standard aqueous flat cell (Decca Radar Ltd.), but later, cells of various thicknesses of up to 2 mm optical pathlength were used and these were constructed in the Departmental Workshops by Mr. K. Holden. Such a cell is shown in figure 6 (b).

The temperature of the solutions flowing through the cell was regulated by blowing cold nitrogen gas through the cell, thereby cooling the incoming liquid. By passing the nitrogen gas through a copper coil immersed in liquid nitrogen and varying the flow of this cold gas through the cell, the temperature of the flowing liquid could be varied. The crudity of this control system soon became apparent, for fluctuations in gas pressure could cause excessive cooling of the sample until it froze and cracked the cell, and a number of cells were broken in this manner. The final modification was to fit a heater and a feedback circuit to the nitrogen flow system, thereby maintaining steady temperature control over the system. This was accomplished by modifying the Decca variable temperature insert to accept the flow cell. The feedback and heater circuit used the standard temperature controller component (Decca Radar Ltd.).

A typical experimental procedure is as follows. Solutions of metal ion ($\sim 5 \times 10^{-3} \text{ M}$) and substrate (up to 1M) were prepared and degassed as described in chapter 2 (page 27). The syringes were removed from the outgassing rig, positioned in the flow system and the motor started. Gradually the temperature of the cell was lowered to within a few degrees of the freezing point of the solvent. The cavity was tuned and the photolysis lamp brought up and focussed on the cavity. Even with the heat filter fitted, the temperature of the cavity tended to rise a few degrees and this was corrected by use of the temperature controller to obtain optimum conditions.

7.2 Results

7.2.1. Ce^{IV} Photo-Oxidation of Alcohols

Methanol - Photolysis of solutions of ceric ammonium nitrate in methanol at a variety of concentrations, varying from 10^{-4} to 10^{-2} M produced no observable spectra. The addition of water ($\sim 5\%$) also had no effect. This therefore provided a useful universal solvent for the low temperature flow method. There are a number of reasons why methanol does not give a spectrum: possibly the production of CH_2OH (formed in the solid state) has a low quantum yield or perhaps rapid oxidation of CH_2OH by Ce^{IV} could also occur and in this case no spectra would be observed, the products being diamagnetic.

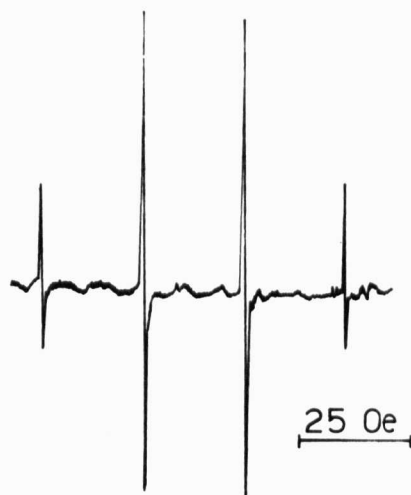
Ethanol - Photolysis of solutions of ceric ammonium nitrate in aqueous (5%) ethanol at 182°K led to the production of a well-resolved 1:3:3:1 quartet with $a_{\text{H}} = 22.91 \text{ Oe}$ identified as $\text{CH}_3\dot{\text{C}}$ (fig. 27 (a)). Variations in concentration of metal ion from 10^{-4} to $5 \times 10^{-2} \text{ M}$ produced no change in the spectra observed, but some reduction in signal intensity was noted with higher Ce^{IV} concentrations, presumably due to increased radical oxidation by Ce^{IV} species, and the optimum metal ion concentration was found to be $\sim 5 \times 10^{-3} \text{ M}$. The lack of spectra attributable to $\text{CH}_3\dot{\text{C}}\text{HOH}$ is in complete contrast to the results obtained at 77°K where the main species produced was $\text{CH}_3\dot{\text{C}}\text{HOH}$ (although some $\text{CH}_3\dot{\text{C}}$ is produced as a minor species at 77°K). The experiment was repeated, using ceric perchlorate as oxidising agent, to rule out the possibility of oxidation by NO_3^\cdot proposed by Martin;⁶⁸ apart from a slow thermal reaction between Ce^{IV} and ethanol, the results were exactly the same as before, i.e. production of $\text{CH}_3\dot{\text{C}}$.

Propan-1-ol - Examination of a cold solution of ceric ammonium nitrate

FIGURE 27

**E.S.R. Spectra Obtained During Photo-Oxidation of
Alcohols in the Liquid Phase by Ce^{IV}**

- (a) Ethanol at 182°K**
- (b) Propanol at 190°K**
- (c) Butanol at 194°K**



(a)



(b)



(c)

(5×10^{-3} M) in aqueous (5%) propan-1-ol under intense photolysis at 190°K yielded the spectrum shown in figure 27 (b), assigned to $\text{C}_2\text{H}_5^{\cdot}$ ($a_{\text{CH}_3}^{\text{H}} = 26.69$ Oe, $a_{\text{CH}_2}^{\text{H}} = 22.25$ Oe).

Butan-1-ol - Although butan-1-ol freezes at 184°K it was possible to carry out observations at 194°K with good results. The spectrum shown in figure 27 (c) is assigned to $\text{CH}_3\text{CH}_2\text{CH}_2^{\cdot}$ radical with $a_{\text{CH}_2(\alpha)}^{\text{H}} = 21.8$ Oe, $a_{\text{CH}_2(\beta)}^{\text{H}} = 29.8$ Oe, $a_{\text{CH}_3}^{\text{H}} < 0.5$ Oe. The signal was of insufficient intensity to allow resolution of the small γ -proton splittings reported to be 0.38 Oe by Fessenden and Schuler¹⁰⁵ who observed the spectrum of $\text{CH}_3\text{CH}_2\text{CH}_2^{\cdot}$ during irradiation of liquid propane.

Pentan-1-ol - Experiments with Ce^{IV} under a variety of conditions produced only a very poor nine-line spectrum analysed in terms of splitting from two protons of 28.5 Oe and a further splitting of 21.8 Oe from two other protons and assigned to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^{\cdot}$. The poor quality of the spectrum was perhaps due to the relatively high temperature (210°K) required before the solutions would flow through the cell.

Isopropanol - Examination by the standard flow method produced a poor spectrum of CH_3^{\cdot} with $a_{\text{H}} = 22.9$ Oe at 200°K .

7.2.2. Ce^{IV} Photo-Oxidation of Carboxylic Acids

Acetic Acid - Photolysis of a solution of acetic acid (2 M) in methanol and ceric ammonium nitrate (5×10^{-3} M) at 190°K yielded the now well-known four-line spectrum of CH_3^{\cdot} ($a_{\text{H}} = 22.9$ Oe). Clearly the same process occurring at 77°K is still operating at 190°K .

Propionic Acid - Examination at 180°K of a methanolic solution of ceric ammonium nitrate and propionic acid yielded a twelve-line spectrum attributable to $\text{C}_2\text{H}_5^{\cdot}$ with $a_{\text{CH}_3}^{\text{H}} = 26.5$, $a_{\text{CH}_2}^{\text{H}} = 22.0$, comparing well with those obtained by Fessenden and Schuler ($a_{\text{CH}_3}^{\text{H}} = 26.9$, $a_{\text{CH}_2}^{\text{H}} = 22.4$ Oe).

Isobutyric Acid - Investigation in a similar manner to the other acids produced at 190°K the spectrum shown in figure 28 (a), consisting of ten lines and assigned to the isopropyl radical $(\text{CH}_3)_2\text{CH}^{\cdot}$ with $a_{\text{CH}_3}^{\text{H}} = 24.6$, $a_{\text{CH}}^{\text{H}} = 22.0$ Oe, the outer group of lines being buried in the noise. Some second-order structure is just observable on some of the centre lines, causing a reduction in intensity from the normal binomial distribution.

Pivalic Acid - The spectrum shown in figure 28 (b) was obtained at 195°K

FIGURE 28

**E.S.R. Spectra Obtained During Photo-Oxidation of
Acids in Methanolic Solution by Ce^{IV}**

- (a) Isobutyric Acid at 190°K**
- (b) Pivalic Acid at 195°K**
- (c) Resolution of second order effects on
the fifth line of the tert-butyl radical**



(a)



(c)



(b)

and is analysed in terms of coupling from nine equivalent protons with $a_H = 21.97$ Oe and assigned to the tertiary butyl radical $(CH_3)_3\dot{C}$ in good agreement with other values for this radical. The signal-to-noise ratio is too low to enable resolution of the wing peaks, the intensity of the middle lines being one hundred and twenty-six times greater than the first line. Examination of the fifth line of the spectrum (figure 28(c)) under conditions of low modulation amplitude revealed the well-resolved second-order structure of this line. The intensities of the four observable lines are 8:28:49:36 and splittings 0.23, 0.63, 1.17 Oe, in fair agreement with the theoretical values¹⁰⁶ of 1:8:27:48:42 for the intensities (the first line of our spectrum being too weak to be observed) and 0.24, 0.71, 1.42 Oe for the splittings.

Lactic Acid, Trifluoroacetic Acid - These acids failed to produce any observable spectra.

7.2.3. U^{VI} Photo-Oxidation of Some Organic Compounds

Methanol - Photolysis of a solution of uranyl perchlorate (5×10^{-3} M) in neat degassed methanol at 215°K produced a spectrum attributed to $\dot{C}H_2OH$ with $a_{CH_2}^H = 17.60$ Oe, $a_{OH}^H = 1.94$ Oe. Cooling to 200°K gave an increase in resolution and the spectrum shown in figure 29(a) was observed at 195°K. Photolysis of aqueous (5%) solutions yielded lower radical concentrations. This mode of photo-oxidation is in complete agreement with that observed at 77°K (page 68). The radical $\dot{C}H_2OH$ is known to exhibit alternating line-width effects¹²⁹ and as the temperature was lowered, the intensity of the two middle lines decreased with respect to the outer lines. The temperature at which both protons appear inequivalent was never reached due to the solution freezing.

Ethanol - The spectrum shown in figure 29(b) was obtained when a solution of uranyl perchlorate (5×10^{-3} M) in neat degassed ethanol was photolysed at 185°K in the flow system. Clearly the ethanol complex of U^{VI} decomposes to give $\dot{C}H_3CHOH$ with $a_{CH_3}^H = 22.9$, $a_{CH}^H = 15.8$, $a_{OH}^H = 1.56$ Oe. Other values for this radical were 22.7, 15.5 and 0.98 respectively.¹²⁰

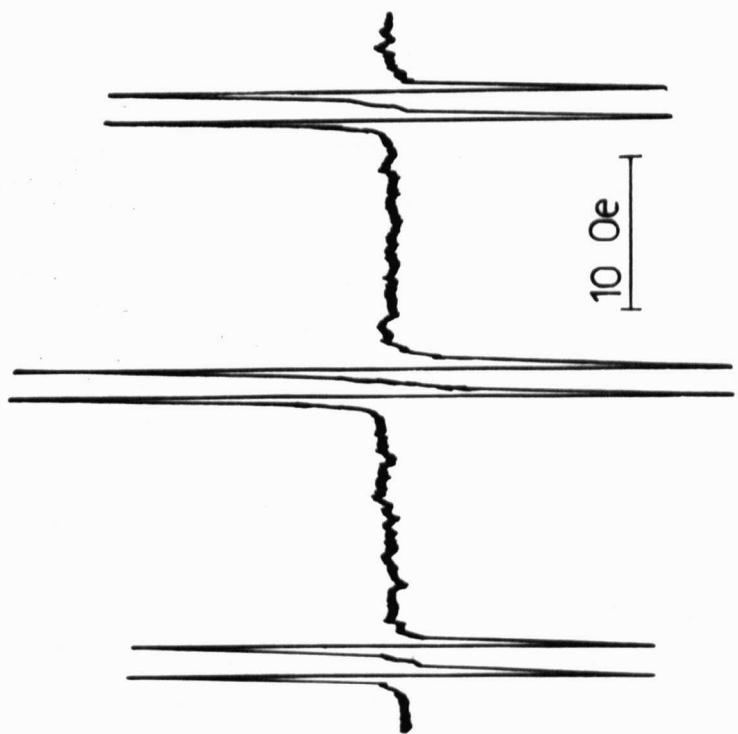
Propan-1-ol - Investigation by the usual flow method at 180°K yielded a poor spectrum consisting of six main broad lines and analysed as $\dot{C}H_3CH_2\dot{C}HOH$ with $a_{CH_2}^H = 22.0$, $a_{CH}^H = 15.4$ Oe. Variations in concentration of U^{VI} and flow rate, all failed to produce any enhancement in resolution. A similar effect was noted with this radical, formed by photolysis of a solution of H_2O_2 and propanol

FIGURE 29

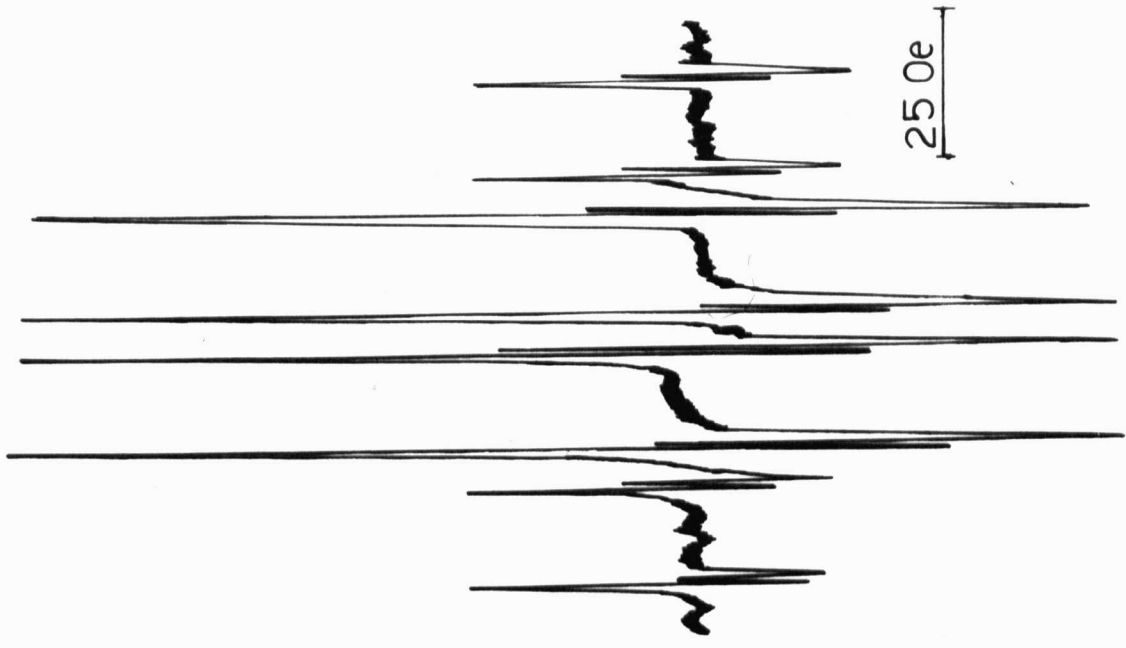
**E.S.R. Spectra Obtained During Photo-Oxidation of
Alcohols by U^{VI} in the Liquid State**

(a) Methanol at $195^{\circ}K$

(b) Ethanol at $185^{\circ}K$



(a)

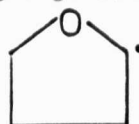


(b)

at 300°K, by Livingston and Zeldes, presumably due to line broadening effects of hindered rotation. Warming to 220°K produced some slight increase in resolution and this was the highest temperature at which the radical was observed.

Propan-2-ol - Experiments with propan-2-ol failed to produce any observable spectra.

Tetrahydrofuran - Photolysis of a solution of uranyl perchlorate (5×10^{-3} M) in neat degassed tetrahydrofuran in a flat cell of 2 mm pathlength at 245°K, produced a complex spectrum consisting of six groups of lines of approximate intensities 1:1:2:2:1:1 and analysed as the



radical with $a_{\alpha}^H = 13.4$ (1 proton), $a_{\beta}^H = 28.2$, $a_{\gamma}^H = 1.0$, $a_{\gamma'}^H = 1.9$ Oe (all for 2 protons). The two end groups at high field are shown in figure 30, together with a computer simulation, based on the above coupling constants. A room temperature spectrum of this radical produced by oxidation with the Ti^{3+}/H_2O_2 couple in a rapid flow system¹¹⁰ gave $a_{\alpha}^H = 12.4$, $a_{\beta}^H = 28.2$, $a_{\gamma}^H = 0.9$, $a_{\gamma'}^H = 1.8$ Oe, in reasonable agreement with our own values.

7.2.4. Photo-Oxidations by Other Metal Ions

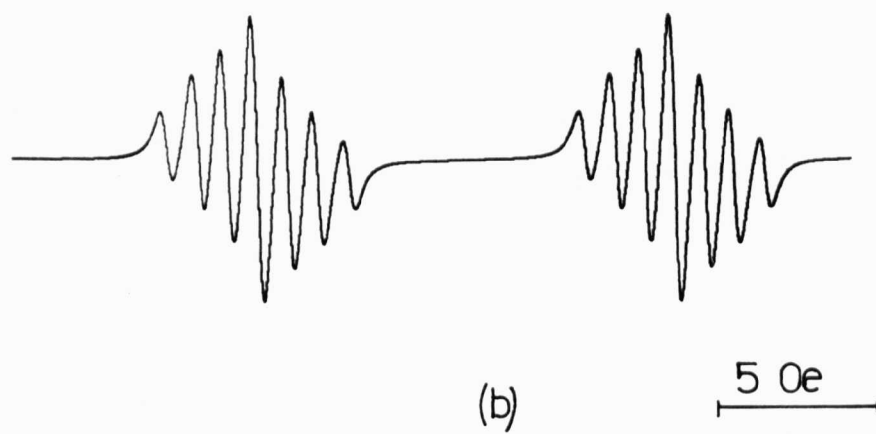
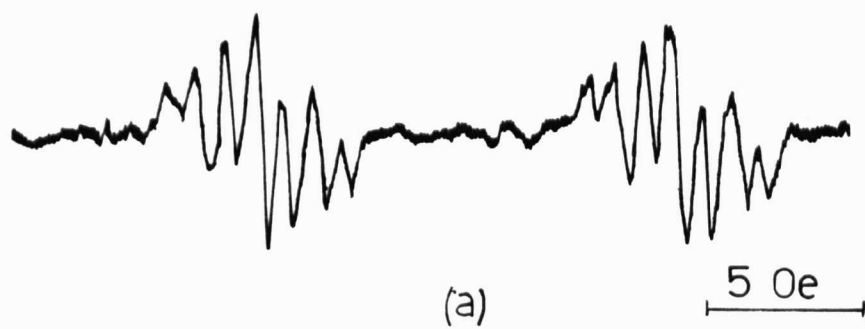
Preliminary work with a number of other metal ions like Fe^{III} and Cu^{II} in the solid state once again showed electron-transfer processes to occur under suitable irradiation conditions, and the following experiments were performed with benzilic acid in the cold flow system.

Benzilic Acid - When a solution of benzilic acid (10^{-2} M) and ferric perchlorate (10^{-3} M) was photolysed with $\lambda > 300$ nm at 185°K in conjunction with the e.s.r. technique described earlier (page 82), a complex spectrum was produced which was analysed as that of the benzophenone ketyl radical Ph_2COH with $a_{3,5,3',5'}^H = 1.24$, $a_{4,4'}^H = 3.70$, $a_{OH} = 2.32$ Oe (all ± 0.01 Oe), in good agreement with the couplings observed by Wilson¹⁹⁶ who examined Ph_2COH by photolysing benzophenone in various solvents with a similar irradiation facility.

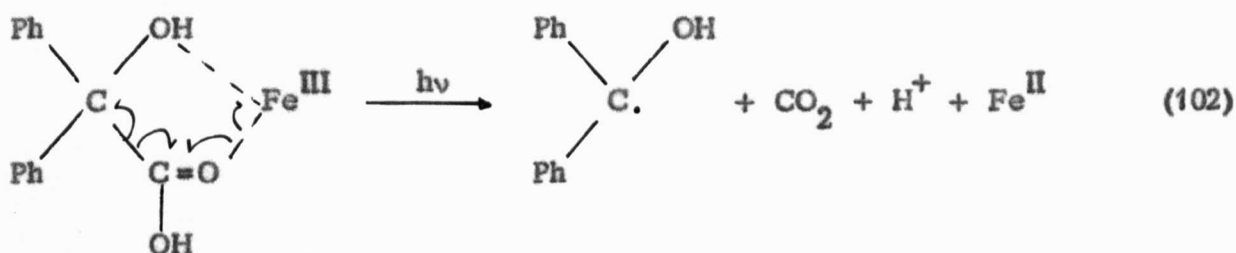
To ascertain the time scale of production of Ph_2COH solutions of benzilic acid and various metal ions (Fe^{III} , U^{VI} , V^V and Cu^{II}) were flash photolysed with light of $\lambda > 300$ nm. (I wish to thank Dr. H. D. Burrows who performed these flash photolysis experiments). The optical spectrum obtained spectrographically with U^{VI} 1 μ sec after the flash (1.1 kJ, $\sim 25 \mu$ s) shown in figure 31 is identical

FIGURE 30

- (a) E.S.R. Spectrum Obtained During Photo-Oxidation
of T.H.F. by U^{VI} at 245°K (end two groups only),
(b) Computer Simulation



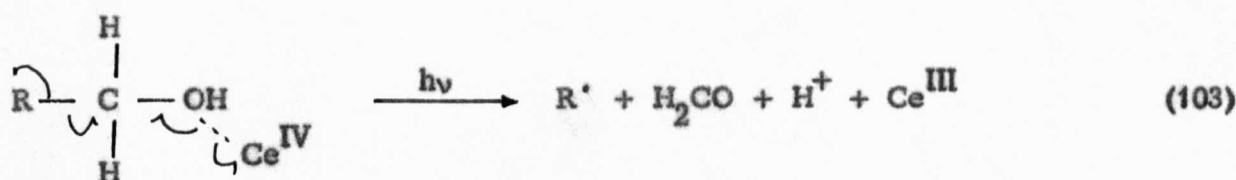
with that given by Porter and Wilkinson.¹⁹⁷ The other metal ions behaved in a similar manner. Benzilic acid alone gave no transient absorption when flashed with light of $\lambda > 300$ nm and addition of 10^{-2} M naphthalene which would have quenched any process of abstraction by benzophenone¹⁹⁷ impurity in the benzilic acid, was without any effect on any of these systems. In both the e.s.r. and flash photolysis experiments, the substrate is subjected to oxidative decarboxylation by the complexed oxidant, viz.



DISCUSSION AND SUGGESTIONS FOR FURTHER WORK

Alcohols

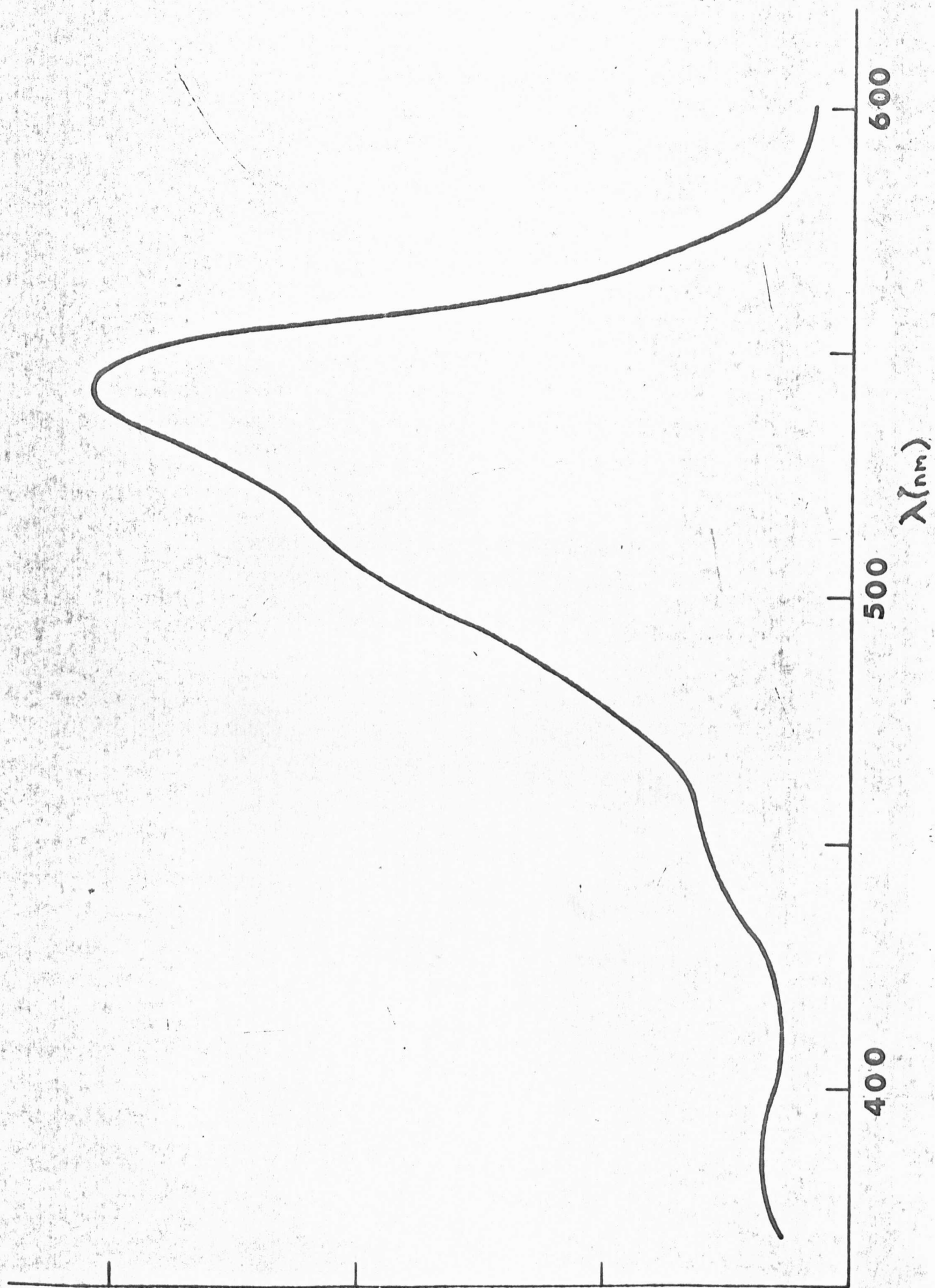
The most striking observation with the alcohols is the production of alkyl radicals rather than the alcohol radicals ($\text{RCHOH}\cdot$) from RCH_2OH during photo-oxidation in solution by Ce^{IV} , contrasting strongly with the behaviour at 77°K where the main radicals produced are $\text{RCHOH}\cdot$ formed by an α -hydrogen atom abstraction mechanism. Assuming that hydrogen abstraction occurs as the primary process in solution, then it is not difficult to see how alkyl radicals could be produced. Initial oxidation of RCHOH by Ce^{IV} to the carbonium ion (RCHOH^+) is followed by subsequent loss of a proton to yield the aldehyde RCHO , which is itself rapidly photo-oxidised by further Ce^{IV} to give $\text{R}\cdot$ (as observed in the solid state - see chapter 5). It is also possible that alkyl radicals could be produced in an initial concerted mechanism, viz.



in a similar manner to the mechanism of oxidation of tertiary alcohols by Ce^{IV} (page 33), implying a difference in activation energies between reaction (103) and production of $\text{RCHOH}\cdot$. Assuming production of $\text{RCHOH}\cdot$ to be an effectively zero

FIGURE 31

Flash Photolysis Spectrum Obtained from a
Solution in Ethanol of Uranyl Perchlorate
(2×10^{-3} M) and Benzilic Acid (2×10^{-3} M)



activation energy process, then these radicals will predominate in the solid state. At higher temperatures in solution reaction (103) becomes important.

The photo-oxidations of U^{VI} in solution at $200^{\circ}K$ are in accord with those observed at $77^{\circ}K$. The spectra produced, however, are better-resolved due to averaging-out of the dipolar interactions. One interesting point to note in the U^{VI} solution work is the appearance of radicals at relatively high temperatures, i.e. compared with Ce^{IV} solutions, presumably because the oxidation of the radicals by U^{VI} or U^V is slower than that by Ce^{IV} , in keeping with the differences in oxidation potentials.

The final observations with Fe^{III} show the versatility of this technique in studying the photochemistry of redox systems in solution, and points the way to a new area of work. Summarising briefly the work pursued so far; we have studied electron-transfer reactions initially with favourable systems by using Ce^{IV} and alcohols, irradiating in the intense charge-transfer band and stabilising the products by the matrix isolation method, and have subsequently extended the work using Ce^{IV} to a wide variety of organic compounds. Having established the technique, some reactions of U^{VI} have been studied at $77^{\circ}K$. The work has been further extended to study photo-oxidation reactions in solution with some degree of success.

Further work is obviously required with the cold flow system and here the possibilities seem great. The correct combination of oxidant, solvent and substrate should allow the study of any primary processes in photo-redox chemistry. So far, electron-transfer reactions between metal ion and organic substrates have been discussed, but there is no reason why the work with the milder thermal oxidants like Fe^{III} and U^{VI} should not be extended to the realm of inorganic substrates, thereby generating inorganic radicals with a specificity rather greater than the present method of γ - and X-irradiation of appropriate solids which often produces a number of radical intermediates. A number of these experiments were attempted with Ce^{IV} , but hydrolysis and precipitation occurred, making sample preparation difficult. The use of this technique to study polymerisation reactions has been demonstrated in chapters 5 and 6 in the case of acrylic acids.

APPENDICES

APPENDIX 1

EXPERIMENTAL

Preparation of Ceric Perchlorate - A.R. ceric ammonium nitrate was used. Solutions of Ce^{IV} in perchloric acid were prepared as follows : concentrated aqueous ceric ammonium nitrate was treated with 0.880 ammonia until precipitation of the basic oxide had ceased. The oxide was separated in a sintered glass funnel and washed with much distilled water and finally dissolved in 60% perchloric acid (A.R. grade).

Lactic acid - This was purified by fractional distillation under reduced pressure.¹⁹⁸

Formic acid - purified by distillation through a 90 cm column at reduced pressure into a receiver cooled with ice,¹⁹⁸ followed by pumping for six hours at 279°K and 10^{-6} mm to remove any formaldehyde, acetaldehyde, etc.

Acrylic, Methacrylic acids - Vacuum distilled through a column packed with copper gauze to remove inhibitors.¹⁹⁸

Phenylacetaldehyde - The monomer was distilled from a partly polymeric sample (B.D.H.) under reduced pressure immediately prior to examination.

T.H.F. and Diethylether - distilled freshly for each experiment.

2,2',4,4'-Tetradeuteropentan-3-one - This was prepared by refluxing repeatedly for 24 hours in a sealed system, mixtures of D_2O , potassium bicarbonate and the parent proton compound¹⁹⁹ until the deuteration was greater than 95% by n.m.r. The product was separated and distilled before use.

Unless otherwise stated, all the substrates used were best quality available and studied without further purification.

APPENDIX 2

The programme ESRTEST enables the computation and simulation of an experimental e.s.r. spectrum. Having been fed with the coupling constants, together with the spin and number of atoms comprising each magnetically equivalent group, calculation of line positions and relative intensities ensues, with subsequent sorting of the lines into their correct positions. A further procedure, based on a Lorentzian line-shape function, enables graphical simulation of the spectrum, hence giving a direct check of the interpretation of the experimental spectrum.

The input data are as follows :

CHOICE	0 if only tabular output is required and 1 for graphical presentation.
CONFAC	Conversion factor in oersted per centimetre, which allows all measured data to be input in centimetres while output in oersteds is obtained.
CWID	Peak-to-peak line width.
HTE	Peak-to-peak height of the largest line. This factor allows scaling of the simulated spectrum to the experimental one.
N	The number of magnetically non-equivalent groups in the molecule in question.

For each group of magnetic nuclei the following data are input :

NO[M]	The number of equivalent nuclei.
SP[M]	Twice the spin for the nucleus.
CA[M]	The coupling constant for the group.

The tabulated output gives the line width and, for each group of equivalent nuclei, the number of nuclei, their spin and the coupling constant. This is followed by the position of each line, relative to the centre of the spectrum, and for each line, its degeneracy or relative intensity and the group spin quantum numbers by which its position is determined.

The programme in Algol, is presented overleaf.

ESRTEST;

"COMMENT" IN THE PROGRAM, CHOICE=1 IF THE PLOTTER IS REQUIRED, AND ZERO OTHERWISE. CONFAC IS THE CONVERSION FACTOR IN GAUSS/CM. HITE IS STRICTLY THE PRODUCT OF THE HEIGHT OF THE FIRST LINE AND THE MAXIMUM DEGENERACY, THUS ALLOWING FOR ACCIDENTAL DEGENERACIES, BUT NORMALLY THE HEIGHT OF THE LARGEST LINE WILL DO: MEASURED IN CENTIMETRES. CWID IS THE PEAK-PEAK LINE WIDTH, MEASURED IN CENTIMETRES. N IS THE NUMBER OF DIFFERENT GROUPS IN THE MOLECULE IN QUESTION, AND FOR EACH GROUP NO IS THE NUMBER OF ATOMS, SP IS TWICE THEIR SPIN AND A IS THE SPLITTING CONSTANT, MEASURED IN CENTIMETRES;

"BEGIN" "INTEGER" N, XX, MOVE, CHOICE, FINAL;

"REAL" Y, YP, YY, RX, WIDTH, CWID, CONFAC, HMAX,

T, DEN, NEWPL, IGNORE, HITE;

"READ" CHOICE, CONFAC, CWID, HITE;

"IF" CHOICE=0 "THEN" "GOTO" OK; "IF" CHOICE=1 "THEN" "GOTO" OK;

"PRINT" 'YOU FORGOT THE VARIABLE THAT SELECTS WHETHER OR NOT YOU USE THE GRAPH PLOTTER'; "GOTO" ERROR; OK;

"PRINT" 'S7*ATOM*S4*NO IN GROUP*S7*SPIN',

SAMELINE, 'S7*SPLITTING CONSTANT*S8*LINE WIDTH';

"PRINT" 'L1S45*CMS*S8*GAUSS*S7*CMS*S7*GAUSS';

WIDTH:=CWID/1.27;

"PRINT" 'L2S67', SAMELINE, ALIGNED(1,3), CWID,

'S4', ALIGNED(1,3), CWID*CONFAC;

"READ" N;

"BEGIN" "INTEGER" "ARRAY" BLIM, NO, SP, LIMIT[1:N];

"REAL" "ARRAY" A[1:N], CA[1:N];

"INTEGER" M, L, BLIMAX, LIMAX, J, I, Z, P, K, X, CH, ML;

"REAL" CHANGE;

LIMAX:=BLIMAX:=0; ML:=1;

"PRINT" 'L2'; "FOR" M:=1 "STEP" 1 "UNTIL" N "DO"

"BEGIN" "READ" NO[M], SP[M], CA[M];

A[M]:=CA[M]/2.54;

"PRINT" 'L1', M, SAMELINE, 'S4', NO[M],

'S11', ALIGNED(1,1), SP[M]/2, 'S5', ALIGNED(3,3), CA[M],

'S4', ALIGNED(3,3), CA[M]*CONFAC;

BLIM[M]:=(SP[M]+1)*NO[M];

"IF" BLIM[M]> BLIMAX "THEN" BLIMAX:= BLIM[M];

LIMIT[M]:= SP[M]* NO[M] +1;

"IF" LIMIT[M] > LIMAX "THEN" LIMAX:= LIMIT[M];

ML:=ML* LIMIT[M]; "END";

"BEGIN" "INTEGER" "ARRAY" AA[1:N,1:BLIMAX], LL, H[1:N,1:LIMAX],

HT,QQ[0:N,1:ML];

"REAL" "ARRAY" PL[0:N,1:ML];

"INTEGER" O, MAX, LIMIT, TEST, SCOPE, R, F, D, E, MAXI, SPIN;

"FOR" M:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN" "COMMENT" WE FIND ALL POSS-
-IBLE NUCLEAR SPIN CONFIGURATIONS FOR EACH GROUP;

"INTEGER" "ARRAY" B[0:NO[M],1:BLIM[M]];

B[0,1]:= 0; F:= D:= E:= MAXI:=1;

NEWROW: SPIN:= -SP[M];

ADD: "IF" SPIN=SP[M]+ 2 "THEN" "BEGIN" F:=F+1;

SPIN:= -SP[M]; "END";

"IF" F> MAXI "THEN" "GOTO" NEWDEE;

B[D,E]:= B[D-1,F] + SPIN;

E:= E+1; SPIN:= SPIN + 2; "GOTO" ADD;

NEWDEE: "IF" D= NO[M] "THEN" "GOTO" CONDENSE;

MAXI:= MAXI * (SP[M] + 1); D:= D+1; E:= F:= 1; "GOTO" NEWROW;

CONDENSE: "FOR" E:=1 "STEP" 1 "UNTIL" BLIM[M] "DO" AA[M,E]:=B[NO[M],E];

```

J:= I:= Z:=0; NEXT: J:= J+1; NEW: Z:= Z+1;
"IF" Z> BLIM[M] "THEN" "GOTO" MORE;
I:= Z; P:=AA[M,I];
"IF" I =1 "THEN" "GOTO" START;
"FOR" K:=1 "STEP" 1 "UNTIL" Z-1 "DO" "IF"AA[M,K]=AA[M,I] "THEN"
"GOTO" NEW; START: LL[M,J]:= P; H[M,J]:= 1;
"IF" Z= BLIM[M] "THEN" "GOTO" MORE;
"FOR" I:=1+Z "STEP" 1 "UNTIL" BLIM[M] "DO"
"IF"AA[M,I] = P "THEN" H[M,J]:= H[M,J] + 1;
"GOTO" NEXT; MORE: "END";
"COMMENT" NOW WE PUT THE GROUP QUANTUM NUMBERS TOGETHER TO GET
LINE POSITIONS AND DEGENERACIES; L:= J:= 0; M:= 0:= MAX:= 1;
PL[0,1] := 0; HT[0,1] := 1;
CYCLE: LIMIT:= SP[M] * NO[M] + 1; R:=0; TEST:=0 ;
SCOPE:=ML/ (MAX * LIMIT );
INC: "IF" J = LIMIT "THEN" "BEGIN" J:=0; Q:= Q+1;
"END"; "IF" Q > MAX "THEN" "GOTO" LEAP ;
TEST:= TEST + SCOPE;
L:=L+1; J:=J+1;
PL[M,L]:=PL[M-1,Q]+LL[M,J]*A[M];
HT[M,L]:= HT[M-1,Q] * H[M,J];
LABEL: "IF" R= TEST "THEN" "GOTO" INC;
R:= R+1; QQ[M,R]:= LL[M,J]; "GOTO" LABEL ;
LEAP: M:= M+1; MAX:= LIMIT * MAX; L:= J:= 0; Q:=1;
"IF" M>N "THEN" "GOTO" FURTHER; "GOTO" CYCLE;
"COMMENT" NOW WE SORT THE LINES BY POSITION;
FURTHER:
"FOR"X:=ML "STEP" -1 "UNTIL" 2 "DO" "FOR" J:=2 "STEP" 1 "UNTIL" X "DO"
"IF"PL[N,J-1] >PL[N,J] "THEN" "BEGIN"
CHANGE:=PL[N,J-1]; PL[N,J-1]:=PL[N,J]; PL[N,J]:= CHANGE;
CH := HT[N,J-1]; HT[N,J-1]:= HT[N,J]; HT[N,J]:= CH ;
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
CH :=QQ[M,J-1]; QQ[M,J-1]:=QQ[M,J]; QQ[M,J]:= CH ; "END"; "END";
"PRINT" 'L4S6'LINE NO'S9'LINE POSITION'S10'DEGENERACY',
SAMELINE, 'S6'GROUP SPIN QUANTUM NOS'; "PRINT" 'L1S21'CMS'S9'GAUSS';
"PRINT" 'L2S55';
SAMELINE; "FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"PRINT" SAMELINE, 'S1', M; "PRINT" 'L2';
"FOR" J:=1 "STEP" 1 "UNTIL" ML "DO" "BEGIN"
"PRINT" 'L1S1', J, SAMELINE, 'S7', ALIGNED(4,3), PL[N,J]*1.27,
'S4', ALIGNED(4,3), PL[N,J]*CONFAC*1.27, 'S3', HT[N,J], 'S5';
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"PRINT" 'S4', ALIGNED(3,1), QQ[M,J]/2; "END";
"IF" CHOICE=0 "THEN" "GOTO" FINIS; PUNCH(5);
HMAX:=0; "FOR" J:=1 "STEP" 1 "UNTIL" ML "DO" "IF" HT[N,J] > HMAX
"THEN" HMAX:=HT[N,J]; HMAX:=(HMAX*14.72)/HITE; SETORIGIN(1300,1);
MOVEPEN(-4,0);
IGNORE:=WIDTH * 1500.0; FINAL:=PL[N,ML] * 100.0 + 50.0;
"FOR" XX:=0 "STEP" 2 "UNTIL" 2*FINAL "DO" "BEGIN" RX:=XX-FINAL;
Y:=0.0; "FOR" J:=1 "STEP" 1 "UNTIL" ML "DO" "BEGIN"
NEWPL:= PL[N,J] * 100.0;
"IF" ABS(RX-NEWPL) > IGNORE "THEN" "GOTO" CUT;
T:= (0.011547 * (RX-NEWPL)) / WIDTH; DEN:= 1+T*T;
Y:= Y + (T * HT[N,J]) / (DEN *DEN); CUT: "END";
YP:=(1800.0*Y)/HMAX; YY:=-YP; DRAWLINE(XX,YY);
"END"; FINIS: "END"; "END"; ERROR: "END" ;

```


APPENDIX 3

The programme ESRTT2 enables the computation and simulation of any number of superimposed spectra, although for convenience, it has been modified from its general form to simulate two spectra only. The method of solution is as in ESRTTEST and the output is similar, the data being presented separately for each component and also for the mixed spectrum where the lines from both species are sorted by position and the graphical simulation is based upon the final line positions.

The input of data is similar to that for ESRTTEST, but some additional parameters are required, the order being given below :

CHOICE	0 for tabular presentation alone and 1 for tabular presentation and graphical simulation.
MOLNO	The number of component species present ; in this work always two.
CONFAC	Conversion factor.
CENSEP	Separation of the centres of the two component spectra.

For each component the input is then :

INSTRING	The title of the species.
CWID	The peak-to-peak line width.
HTE	The peak-to-peak height of the largest line.
N	The number of magnetically non-equivalent groups.

Again, for each component the input of data for the separate groups of nuclei is :

NO	The number of equivalent nuclei.
SP	Twice the spin of the nucleus.
CA	The coupling constant for the group.

The programme, in Algol, is presented overleaf.

```

                                ESRTT2;
"BEGIN" "INTEGER" CHOICE, MOLNO, XX, MOVE, FINAL, NML, TN, C, 0, J,
M, MM, CHA, NMAX, S, R, BS, GMAX, BMAX, LMAX, MLMAX;
"REAL" RX, CONFAC, CENSEP, CHAN, T, DEN, NEWPL, Y, YY, 00;
"READ" CHOICE, MOLNO, CONFAC, CENSEP;
"IF" CHOICE=0 "THEN" "GOTO" OK; "IF" CHOICE=1 "THEN" "GOTO" OK;
"PRINT" 'YOU FORGOT THE VARIABLE THAT SELECTS WHETHER OR NOT
YOU USE THE GRAPH PLOTTER'; "GOTO" ERROR;
OK:
NML:=0;
"BEGIN" "INTEGER" "ARRAY" N, HMAX[1:MOLNO], HEAD[1:20];
"REAL" "ARRAY" WIDTH, CWID, GWID, HITE, IGNORE, HHMAX[1:MOLNO];
GMAX:=0;
MM:=1;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
INSTRING(HEAD,MM);
"READ" CWID[B], HITE[B], N[B];
GWID[B]:=CWID[B]*CONFAC; WIDTH[B]:=CWID[B]/1.27;
"IF" N[B]>GMAX "THEN" GMAX:=N[B]; "END";
"BEGIN" "INTEGER" "ARRAY" BLIM, LIMIT, NO, SP[1:MOLNO,1:GMAX],
ML, BLIMAX, LIMAX[1:MOLNO];
"REAL" "ARRAY" A, GA, CA[1:MOLNO,1:GMAX];
"INTEGER" L, I, Z, P, K, X, CH;
"REAL" CHANGE;
LMAX:=BMAX:=MLMAX:=0;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
LIMAX[B]:=BLIMAX[B]:=0; ML[B]:=1;
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"BEGIN" "READ" NO[B,M], SP[B,M], CA[B,M];
GA[B,M]:=CA[B,M]*CONFAC; A[B,M]:=CA[B,M]/2.54;
BLIM[B,M]:=(SP[B,M]+1)*NO[B,M];
"IF" BLIM[B,M]>BLIMAX[B] "THEN" BLIMAX[B]:=BLIM[B,M];
"IF" BLIMAX[B]>BMAX "THEN" BMAX:=BLIMAX[B];
LIMIT[B,M]:=SP[B,M]*NO[B,M]+1;
"IF" LIMIT[B,M]>LIMAX[B] "THEN" LIMAX[B]:=LIMIT[B,M];
"IF" LIMAX[B]>LMAX "THEN" LMAX:=LIMAX[B];
ML[B]:=ML[B]*LIMIT[B,M];
"IF" ML[B]>MLMAX "THEN" MLMAX:=ML[B];
"END"; "END";
C:=ML[1];
NML:=NML+ML[1]+ML[2];
00:=ABS(CENSEP);
"PRINT" 'L2S10`SPECTRA SEPERATION`S1`, SAMELINE, ALIGNED(1,3), 00,
'S1`CMS`S3`, ALIGNED(1,3), 00*CONFAC, 'S1`GAUSS`;
"PRINT" 'L2S10`RELATIVE INTENSITIES`S1`;
"IF" HITE[1]"GE" HITE[2] "THEN" "BEGIN"
00:=HITE[1]/HITE[2];
"PRINT" SAMELINE, ALIGNED(3,3), 00, 'S1`1:2`; "END" "ELSE" "BEGIN"
00:=HITE[2]/HITE[1];
"PRINT" SAMELINE, ALIGNED(3,3), 00, 'S1`2:1`; "END";
"BEGIN" "INTEGER" "ARRAY" AA[1:GMAX,1:BMAX], LL,
HC[1:GMAX,1:LMAX], HT, QQ[1:MOLNO,0:GMAX,1:MLMAX], LIMIT[1:MOLNO],
DT, SS[1:NML], DO, TO[0:GMAX, 1:NML];
"REAL" "ARRAY" PL[1:MOLNO,0:GMAX,1:MLMAX],
DL[1:NML];
"INTEGER" Q, MAX, TEST, SCOPE, R, F, D, E, MAXI, SPIN;

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"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" "BEGIN"
"COMMENT" WE FIND ALL POSSIBLE NUCLEAR SPIN CONFIGURATIONS
FOR EACH GROUP;
"INTEGER" "ARRAY" BB[0:NO[B,M], 1:BLIM[B,M]];
BB[0,1]:=0; F:=D:=E:=MAXI:=1;
NEWROW: SPIN:=-SP[B,M];
ADD: "IF" SPIN=SP[B,M]+2 "THEN" "BEGIN" F:=F+1; SPIN:=-SP[B,M]; "END";
"IF" F>MAXI "THEN" "GOTO" NEWDEE;
BB[D,E]:=BB[D-1, F]+SPIN;
E:=E+1; SPIN:=SPIN+2; "GOTO" ADD;
NEWDEE: "IF" D=NO[B,M] "THEN" "GOTO" CONDENSE;
MAXI:=MAXI*(SP[B,M]+1); D:=D+1; E:=F:=1; "GOTO" NEWROW;
CONDENSE: "FOR" E:=1 "STEP" 1 "UNTIL" BLIM[B,M] "DO"
AA[M,E]:=BB[NO[B,M], E];
J:=I:=Z:=0;
NEXT: J:=J+1;
NEW: Z:=Z+1;
"IF" Z>BLIM[B,M] "THEN" "GOTO" MORE;
I:=Z; P:=AA[M,I];
"IF" I=1 "THEN" "GOTO" START;
"FOR" K:=1 "STEP" 1 "UNTIL" Z-1 "DO"
"IF" AA[M,K]=AA[M,I] "THEN" "GOTO" NEW;
START: LL[M,J]:=P; H[M,J]:=1;
"IF" Z=BLIM[B,M] "THEN" "GOTO" MORE;
"FOR" I:=1+Z "STEP" 1 "UNTIL" BLIM[B,M] "DO"
"IF" AA[M,I]=P "THEN" H[M,J]:=H[M,J]+1;
"GOTO" NEXT; MORE: "END";
"COMMENT" NOW WE PUT THE GROUP QUANTUM NUMBERS TOGETHER
TO GET THE LINE POSITIONS AND DEGENERACIES;
L:=J:=0; M:=Q:=MAX:=1;
PL[B,0,1]:=0; HT[B,0,1]:=1;
CYCLE: LIMIT[B]:=SP[B,M]*NO[B,M]+1; R:=0; TEST:=0;
SCOPE:=0;
SCOPE:=ML[B]/(MAX*LIMIT[B]);
INC: "IF" J=LIMIT[B] "THEN" "BEGIN" J:=0; Q:=Q+1; "END";
"IF" Q>MAX "THEN" "GOTO" LEAP;
TEST:=TEST+SCOPE;
L:=L+1; J:=J+1;
PL[B,M,L]:=PL[B,M-1,Q]+LL[M,J]*A[B,M];
HT[B,M,L]:=HT[B,M-1,Q]*H[M,J];
LABEL: "IF" R=TEST "THEN" "GOTO" INC;
R:=R+1; QQ[B,M,R]:=LL[M,J]; "GOTO" LABEL;
LEAP: M:=M+1; MAX:=LIMIT[B]*MAX; L:=J:=0; Q:=1;
"IF" M>N[B] "THEN" "GOTO" FURTHER; "GOTO" CYCLE;
"COMMENT" NOW WE SORT THE LINES BY POSITION;
FURTHER: "FOR" X:=ML[B] "STEP" -1 "UNTIL" 2 "DO"
"FOR" J:=2 "STEP" 1 "UNTIL" X "DO"
"IF" PL[B,N[B], J-1]>PL[B,N[B], J] "THEN" "BEGIN"
CHANGE:=PL[B,N[B], J-1]; PL[B, N[B], J-1]:=PL[B, N[B], J];
PL[B, N[B], J]:=CHANGE;
CH:=HT[B, N[B], J-1]; HT[B, N[B], J-1]:=HT[B, N[B], J];
HT[B, N[B], J]:=CH;
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" "BEGIN"
CH:=QQ[B, M, J-1]; QQ[B, M, J-1]:=QQ[B, M, J];

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QQ[B,M,
      =CH;   "END";   "END";   "END";
MM:=1;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
"PRINT" "'L2S20'ESR DATA FOR ";
OUTSTRING(HEAD,MM);
"PRINT" SAMELINE, B, "'L2'";
"PRINT" "'S7'ATOM'S4'NO IN GROUP'S7'SPIN",
SAMELINE, "'S7'SPLITTING CONSTANT'S8'LINE WIDTH";
"PRINT" "'L1S45'CMS'S8'GAUSS'S7'CMS'S7'GAUSS";
"PRINT" "'L2S67'", SAMELINE, ALIGNED(1,3), CWID[B],
"'S4'", ALIGNED(1,3), GWID[B], "'L2'";
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"PRINT" "'L1'", M, SAMELINE, "'S4'", NO[B,M],
"'S11'", ALIGNED(1,1), SP[B,M]/2, "'S5'", ALIGNED(3,3), CA[B,M],
"'S4'", ALIGNED(3,3), GA[B,M];
"PRINT" "'L4S6'LINE NO'S9'LINE POSITION'S10'DEGENERACY",
SAMELINE, "'S6'GROUP SPIN QUANTUM NOS"; "PRINT" "'L1S21'CMS'S9'GAUSS";
"PRINT" "'L2S55'";
SAMELINE; "FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"PRINT" SAMELINE, "'S1'", M; "PRINT" "'L2'";
"FOR" J:=1 "STEP" 1 "UNTIL" ML[B] "DO" "BEGIN"
"PRINT" "'L1S1'", J, SAMELINE, "'S7'",
ALIGNED(4,3), PL[B, N[B], J]*1.27, "'S4'", ALIGNED(4,3),
PL[B, N[B], J]*CONFAC*1.27, "'S3'", HT[B, N[B], J], "'S5'";
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"PRINT" "'S4'", ALIGNED(3,1), QQ[B,M,J]/2; "END"; "END";
"COMMENT" NOW SORT OUT BOTH GROUPS OF LINES BY POSITION;
"PRINT" "'L4S20'COMBINED DATA FOR BOTH MOLECULES'L2'";
"FOR" B:=1 "DO" "BEGIN"
J:=0:=0;
IND1: J:=J+1; O:=O+1; SS[O]:=1;
DL[O]:=PL[B, N[B], J];
DT[O]:=HT[B, N[B], J];
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" DO[M,O]:=QQ[B,M,J];
"IF" J=ML[B] "THEN" "GOTO" OUTD1;
"GOTO" IND1; OUTD1:
"END";
"FOR" B:=2 "DO" "BEGIN"
J:=0; O:=0;
IND2: J:=J+1; O:=O+1; SS[O]:=2;
DL[O]:=PL[B, N[B], J]+(CENSEP/1.27);
DT[O]:=HT[B, N[B], J];
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" DO[M,O]:=QQ[B,M,J];
"IF" J=ML[B] "THEN" "GOTO" OUTD2;
"GOTO" IND2; OUTD2:
"END";
"FOR" IN:=NML "STEP" -1 "UNTIL" 2 "DO"
"FOR" O:=2 "STEP" 1 "UNTIL" IN "DO"
"IF" DL[O-1]>DL[O] "THEN" "BEGIN"
CHAN:=DL[O-1]; DL[O-1]:=DL[O]; DL[O]:=CHAN;
CHA:=DT[O-1]; DT[O-1]:=DT[O]; DT[O]:=CHA;
CHA:=SS[O-1]; SS[O-1]:=SS[O]; SS[O]:=CHA;
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[O-1]] "DO" TO[M,O]:=DO[M,O];
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[O]] "DO" DO[M,O]:=DO[M,O-1];

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"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[0-1]] "DO" DQ[M,0-1]:=TQ[M,0];
"END";
"PRINT" 'L2S6' LINE NO'S9' LINE POSITION'S10' DEGENERACY',
SAMELINE, 'S6' GROUP SPIN QUANTUM NOS'; "PRINT" 'L1S21' CMS'S9' GAUSS';
"PRINT" 'L2S55'; NMAX:=0;
"FOR" R:=1 "STEP" 1 "UNTIL" MOLNO "DO"
"IF" N[R]>NMAX "THEN" NMAX:=N[R];
SAMELINE; "FOR" M :=1 "STEP" 1 "UNTIL" NMAX "DO"
"PRINT" SAMELINE, 'S1', M; "PRINT" 'L2';
O:=0; SORT: O:=O+1;
"PRINT" 'L1S1', SAMELINE, O, 'S7';
"PRINT" SAMELINE, ALIGNED(4,3), DL[0]*1.27, 'S4', ALIGNED(4,3),
DL[0]*CONFAC*1.27, 'S3', DT[0], 'S5';
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[0]] "DO" "PRINT" SAMELINE, 'S4',
ALIGNED(3,1), DQ[M,0]/2;
"PRINT" SAMELINE, 'S5', SS[0];
"IF" O=NML "THEN" "GOTO" OUTSORT;
"GOTO" SORT; OUTSORT:
"IF" CHOICE=0 "THEN" "GOTO" FINIS; PUNCH(5);
"FOR" BS:=1 "STEP" 1 "UNTIL" MOLNO "DO" HMAX[BS]:=0;
"FOR" O:=1 "STEP" 1 "UNTIL" NML "DO" "BEGIN"
BS:=SS[0];
"IF" DT[0]>HMAX[BS] "THEN" HMAX[BS]:=DT[0]; "END";
"FOR" BS:=1 "STEP" 1 "UNTIL" MOLNO "DO"
HHMAX[BS]:=(HMAX[BS]*14.72)/HITE[BS];
SETORIGIN(1300,1); MOVEPEN(-4,0);
"FOR" BS:=1 "STEP" 1 "UNTIL" MOLNO "DO"
IGNORE[BS]:=WIDTH[BS]*1500.0;
FINAL:=ENTIER(DL[NML]*100.0+200.0);
"FOR" XX:=0 "STEP" 2 "UNTIL" 2*FINAL "DO" "BEGIN"
RX:=XX-FINAL; Y:=0.0;
"FOR" O:=1 "STEP" 1 "UNTIL" NML "DO" "BEGIN"
BS:=SS[0];
NEWPL:=DL[0]*100.0;
"IF" ABS(RX-NEWPL)>IGNORE[BS] "THEN" "GOTO" CUT;
T:=(0.011547*(RX-NEWPL))/WIDTH[BS]; DEN:=1+T*T;
Y:=Y+(T*DT[0])/(DEN*DEN*HHMAX[BS]); CUT: "END";
YY:=- (1800.0*Y); DRAWLINE(XX,YY);
"END"; FINIS: "END"; "END"; "END"; ERROR: "END";

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